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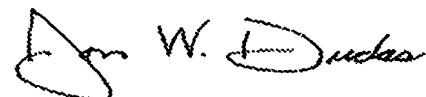
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PROVISIONAL APPLICATION FOR PATENT COVER SHEETThis is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)
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INVENTOR(S)			
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)	
Ammar S. Vicki L. Kevin Matteo Michael S.	Alkhawaldeh Colvin Ausman Pasquali Wong	Houston, TX Houston, TX Houston, TX Houston, TX Houston, TX	
<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto			
TITLE OF THE INVENTION (500 characters max) NEW SOLVENTS AND NEW METHOD FOR THE SYNTHESIS OF CdSe SEMICONDUCTOR NANOCRYSTALS			
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ENCLOSED APPLICATION PARTS (check all that apply)			
<input checked="" type="checkbox"/> Specification	Number of Pages	70	<input type="checkbox"/> CD(s), Number
<input type="checkbox"/> Drawing(s)	Number of Sheets	*	<input type="checkbox"/> Other (specify)
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76			
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT			
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.	FILING FEE		
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.			
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(Page 1 of 1)

Respectfully submitted,

SIGNATURE 

TYPED OR PRINTED NAME Marcella D. Watkin

TELEPHONE (713) 238-8000

Date November 18, 2003

REGISTRATION NO. 36,962

(if appropriate)
DOCKET NO. 1789-13500**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

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NEW SOLVENTS AND NEW METHOD FOR THE SYNTHESIS OF CdSe SEMICONDUCTOR NANOCRYSTALS

FIELD OF THE INVENTION

This invention relates to the synthesis of nanoparticles. Particularly, quantum dots are synthesized using new solvents. More particularly, a nucleation step is separated from growth process by quenching the reaction solution with cold solvent

BACKGROUND OF THE INVENTION

Semiconductor nanocrystals are of great importance for fundamental and application purposes. Optical and electrical properties of quantum dots are size-dependent, which makes them attractive for many applications (Alivisatos, 1996 and Murray et al., 2000). Intensive research has been done in this area in the last few decades. Semiconductor nanocrystals have many potential applications such as quantum dot infrared photodetectors, quantum dot lasers, and photovoltaic devices (Bukowski and Simmons, 2002).

Murray et al. (1993) reported the synthesis of high-quality CdE (E = S, Se, Te) nanocrystals through the rapid injection of organometallic reagents (triptyphosphine selenide [TOPSe], or triptylphosphine telluride [TOPTe] with cadmium source (dimethylcadmium) [Me₂Cd] dissolved in triptylphosphine [TOP]) into a hot coordinating solvent (triptylphosphine oxide [TOPO]) followed by size selective precipitation (Murray et al., 1993 and Katari et al., 1994).

In their work, Dabbousi et al. (1997) described the synthesis and characterization of a series of core-shell (CdSe)ZnS nanocrystals with CdSe cores diameter ranging from 2.3 to 5.5 nm. A quantum yield of (30-50%) and photoluminescence characterized by FWHM of less than 40 nm were achieved. The nanocrystals were synthesized via the pyrolysis of Cd(CH₃)₂ and TOPSe in a coordinating solvent (TOPO) (Dabbousi et al., 1997).

A systematic shape variation (nanorods, arrows, teardrops, and tetrapods) of nanocrystals has been achieved via synthesizing the nanoparticles in a mixture of hexylphosphonic acid and triptylphosphine oxide. The ratio of surfactants, injection volume, and monomer concentration are the main factors in nanoparticle shape control. Ostwald ripening occurs at low monomer

concentrations, whereas at high monomer concentrations the differences in the growth rates of different faces may lead to different shape configurations (Manna et al., 2000).

Peng and Peng (2001) further explored the temporal shape evolution of CdSe nanorods in trioctylphosphine oxide solvent. Nanocrystals grow exclusively along the c-axis of the wurtzite structure at high monomer concentrations, whereas, at intermediate monomer concentrations, the growth is simultaneously in three dimensions. On the other hand, at low monomer concentrations, the intraparticle diffusion on the surface of the nanocrystal decreases the aspect ratio. Moreover, at lower monomer concentrations Ostwald ripening takes place (Peng and Peng, 2001 and Peng et al., 1998).

Duan and Lieber (2000) reported the synthesis of a broad range (III-V, II-VI, and IV-IV) of semiconductor nanowires with diameters ranging from three to tens of nanometers and lengths up to tens of micrometers using laser-assisted growth (Duan and Lieber, 2000).

In an important development, CdSe nanocrystals have been reported to be synthesized using safer and lower cost alternative routes. Fatty acids, amines, phosphine oxides, and phosphonic acids are among those solvent systems used. Moreover, CdO was found to be a more desirable source of cadmium for the synthesis of nanocrystals compared to Cd (CH_3)₂ (Qu et al., 2001). Different varieties of elongated shapes were synthesized using these alternative routes. The magic size nuclei and the concentration of the remaining monomers after the initial nucleation stage are claimed to be the determining factors of the shape configuration of the nanostructured particles (Peng and Peng, 2001). In another study, Qu and Peng (2002) concluded that during the growth of nanocrystals under a given set of initial conditions, photoluminescence quantum yield increases to a maximum value (bright point) before it gradually decreases. This maximum value is said to be a signature of an optimal surface structure (Qu and Peng, 2002)

In an effort to set the basis for developing photoluminescence-based labeling reagents, the chemistry of the CdSe dendron-nanocrystals was investigated. Dendron ligands were used to stabilize CdSe and Au nanocrystals. Hydrophilic organic dendron ligands were designed to

stabilize semiconductor and noble metal nanocrystals by binding onto the surface of the nanocrystal (Wang et. al, 2002).

Recently, Yu and Peng successfully synthesized II-VI semiconductor nanocrystals in non-coordinating solvents. CdS, CdSe, and ZnSe nanocrystals were synthesized in octadecene (ODE) with oleic acid (OA) as a ligand to stabilize the nanocrystals and the cationic precursors. The growth rate of nanocrystals was found to be dependent on the concentration of oleic acid in ODE. As the concentration of OA in ODE increases the growth rate increases (Yu and Peng, 2002)

The choice of solvent for the synthesis of nanocrystals is of great importance, particularly for the purpose of scaling up the production of nanoparticles to achieve commercial nanomanufacturing and mass production. In this work we present new low cost and commercially available solvents for the synthesis of semiconductor nanocrystals, which may have a significant effect on the economic feasibility of commercializing the synthesis of nanoparticles. Dowtherm®, which is a well known heating fluid and a registered trademark of Dow Chemical Company, a Michigan corporation, was used successfully as a solvent to synthesize CdSe quantum dots. Moreover, phenyl ether and biphenyl, which are the constituents of Dowtherm A, were used individually as solvents for the synthesis of CdSe nanocrystals.

Another feature of the present invention is the separation of nucleation and growth through quenching a certain amount of the relatively cold solvent (about room temperature) into the reaction solution immediately after injecting the selenium solution.

DESCRIPTION OF THE INVENTION

a. New Solvent for Quantum Dot Synthesis:

We successfully synthesized CdSe nanocrystals in Dowtherm A (DTA) heating fluid, biphenyl (BP), and phenyl ether (PE). Dowtherm A is “a eutectic mixture of two very stable compounds, biphenyl ($C_{12}H_{10}$) and diphenyl oxide ($C_{12}H_{10}O$)” (See attached Appendix.). The availability and the low cost of Dowtherm A make it an attractive choice for the synthesis of nanoparticles, and particularly for future commercial production. Moreover, Dowtherm A is liquid at room

temperature (m.p. = 12°C), which makes it easier to handle through the synthesis process. Table (1) shows a comparison of the price of Dowtherm A with respect to other solvents.

We adapted the synthesis method of CdSe nanocrystals reported by Yu and Peng (2002) with some changes. Selenium precursor was prepared by dissolving selenium powder into trioctylphosphine (TOP) (Se/TOP = 1/8 molar ratio). CdO was mixed with Dowtherm A fluid (or phenyl ether or biphenyl) and oleic acid (OA) at room temperature (Cd/DTA = 1/300 molar ratio) and (Cd/OA = 1/3 molar ratio). The solution was heated up to 260°C under vigorous stirring for 30 minutes or until the solution cleared up. Selenium solution was swiftly injected into the Dowtherm/CdO/OA solution. The injection temperature was varied from 220 to 260°C, compared to 300°C used by Yu and Peng. CdSe nanocrystals formed as indicated by the change in color for the reaction solution and verified by the UV-Vis and fluorescence spectroscopy analysis.

Figures (1) & (2) show the UV-Vis and fluorescence spectra for the CdSe nanocrystals synthesized in Dowtherm A, biphenyl, or phenyl ether solvents at 160°C. The FWHM of the fluorescence peaks and the particle size of the nanocrystals are shown in Table (2). The FWHM values for CdSe nanocrystals synthesized in these new solvents (DTA, PE, and BP) are comparable to what is reported in the literature for other solvents such as octadecene (ODE) and trioctylphosphine oxide (TOPO). The FWHM is an indication of the monodispersity of the nanoparticles.

Further investigation of the synthesis of CdSe nanocrystals in Dowtherm A solvent is demonstrated in the next section (Quenching Method)

b. Quenching Method

We successfully separated the nucleation step from the growth process by quenching the reaction mixture with relatively cold solvent (at room temperature) immediately after injecting the selenium solution. Injecting the selenium solution at high temperature will start the nucleation of the nanoparticles. Quenching the reaction mixture immediately after the injection will drop the temperature to a level where no more nucleation will take place and no growth of the nucleus will be possible. Temperature will then be raised to the desired level to allow the nucleus to

grow. This method will not only allow us to separate nucleation from growth, but also will allow us to choose the desired growth temperature and as a result choose the desired average particles size.

To further explain this concept, we conducted a set of experiments with different solvents including ODE and Dowtherm A.

ODE/CdO solution was heated up to 300°C under vigorous stirring until the solution cleared. The solution temperature was dropped to 260°C and selenium solution was swiftly injected, followed by quenching the reaction solution with relatively cold (room temperature) ODE (1:1 by volume). The temperature of the reaction solution dropped to 100°C. The reaction solution was kept at 100°C for two hours to monitor any growth by taking aliquots every 30 minutes and analyzing them using the UV-Vis and fluorescence spectroscopy (Figures 3). As demonstrated by Figure (3), a very little (if any) shift in the CdSe absorption peak is observed over the two hours period, indicating that there is virtually no growth at this temperature.

In another experiment, the same steps were followed except that after quenching the reaction solution to 100°C, the temperature was raised to 160°C and kept at that level for two hours to monitor the growth of the particles. The UV-Vis and fluorescence spectra of the samples taken during this period (Figures (4) & (5)) show that nanocrystals grow with time from 2.2 nm immediately after raising the temperature to 160°C to 2.9 nm at the end of the second hour. A product yield (based on Se) as high as 98% and a FWHM as low as 26 nm were achieved (Table 3).

If there were no quenching and the solution were left at an elevated temperature, the particles would grow very quickly and be much larger than particles produced using the present method.

A similar experiment to synthesize CdSe quantum dots in Dowtherm A was conducted using the quenching method. The reaction solution was quenched with cold solvent (Dowtherm A) immediately after injecting the TOPSe solution into the reaction vessel. The temperature dropped to 100°C and was kept at that level for two hours. No significant growth was observed (Figure 6). In another experiment, the same steps were followed except that temperature was

raised from 100 to 160°C immediately after quenching the reaction solution with cold Dowtherm A and was kept at that level for two hours. As illustrated by Figures (7) and (8) the nanoparticles grew with time from 2.1 nm to 3 nm at the end of 2 hours. This shows that quenching the reaction solution with the appropriate amount of cold solvent immediately after introducing the selenium precursor will enable us to separate the nucleation step from the growth process.

POSSIBLE MODIFICATIONS

Our methodology should be extremely amendable to variations, as listed in the following:

1. Different nanoshapes such as but not limited to: rods, arrows, teardrop, tetrapods, ...etc. can be synthesized using Dowtherm A as a solvent. For example, an organic compound such as one or more alkylphosphonates can be added to chemically bind to the surface of the growing particle, thereby affecting the relative growth rates of the crystal faces. As mentioned above, the ratio of surfactants, injection volume, and monomer concentration are factors in nanoparticle shape control. The timing of the addition of additional compounds, as well as that of additional nanoparticle precursors, to the reaction medium post-quenching should be controlled in order to optimize the desired results. Optimum timing can be determined by theoretical or computational modeling or by experimentation.
2. Cadmium sulfide (CdS) nanoparticles and cadmium telluride (CdTe) nanoparticles can be synthesized in Dowtherm A as a solvent.
3. Dowtherm G instead of Dowtherm A can be used as a solvent for the synthesis of quantum dots (Table 4)
4. Dowtherm RP, Dowtherm Q, Dowtherm J, Dowtherm HT, Dowtherm T, or Dowtherm MX can be used instead of Dowtherm A as a solvent for the synthesis of quantum dots
5. Solvents with molecular structures similar to the above-listed solvents are expected to provide similar results. Suitable solvents have a high boiling point, are relatively inert, i.e. meaning having a high decomposition temperature, and are preferably but not necessarily liquid at room temperature. The molecular structure of the solvent molecule preferably provides the above attributes; additional attributes, such as reactive functional groups, are still more preferred. While the solvents mentioned above are organic, inorganic solvents, such as silicone oil and related siloxane compounds (molecule

backbone is composed of Si-O-Si bonds), would also work (they satisfy the above criteria). Fluorinated solvents are also expected to work. Another example of suitable solvents are phenylated compounds, such as triphenyl.

6. The initial high-temperature stage ("nucleation step") can be separated from the lower-temperature stage ("growth step") by quenching the reaction solution with any combination of the-above solvents. Alternatively, quenching can be accomplished by any other suitable means, including but not limited to quenching with a liquid that is immiscible in the solvent, or by contact with a cooling coil, heat sink, or other heat exchanger. Any method that decreases the temperature of the solution abruptly, preferably in seconds, without chemically interacting with the reactants will work. It is preferred that the selected quenching mechanism produce as few inhomogeneities in the local precursor concentrations and in local temperature as possible. Ideally, the reactor is as well-mixed as possible.
7. Metal nanoparticles can be synthesized using these new solvents and/or quenching methods. In this embodiment, the metal chalcogenide precursors are replaced with metal precursors and a reducing agent.
8. Likewise, metal oxide nanoparticles can be synthesized using these new solvents and/or quenching methods by replacing the metal chalcogenide precursors with metal precursors.
9. Other metal chalcogenide nanoparticles besides CdS, CdSe, and CdTe synthesized using these new solvents and/or quenching methods. Examples include: PbSe, PbTe, ZnS, ZnSe → II/VI compositions; GaAs, InSb → III/V compositions
10. Also, we expect to be able to synthesize "core/shell" nanoparticles and related materials using the present techniques. These nanoparticles have a variable coating of another composition, e.g., CdSe nanoparticles with a surrounding shell of CdS are CdSe/CdS core/shell quantum dots. The present techniques can also be used to produce multiple layers.

The present techniques offer several advantages over previously known techniques. These include:

1. Significantly lower priced, commercially available, and "greener" solvents for the synthesis of nanoparticles

2. Separation between nucleation step and growth process by quenching the reaction solution with cold solvent. What advantage does this provide?
3. Better control of the nanoparticles growth temperature
4. Better control of the particle size

What is claimed is:

1. A method for making semiconductor nanocrystals, comprising:
 - a) dissolving a precursor of a desired element in a first solvent to form a precursor solution;
 - b) mixing a metal oxide with a second solvent to form mixture;
 - c) heating the mixture to a predetermined temperature; and
 - d) injecting the precursor solution into the heated mixture to form a growth solution.
2. The method according to claim 1 wherein the first solvent comprises Dowtherm A fluid (or phenyl ether or biphenyl).
3. The method according to claim 2 wherein the first solvent further comprises oleic acid (OA).
4. The method according to claim 1 wherein the first solvent is at room temperature.
5. The method according to claim 1 wherein the precursor solution comprises a molar ratio of the desired element to the first solvent of 1/300.
6. The method according to claim 1 wherein the precursor solution comprises a molar ratio of the desired element to oleic acid of 1/3.
7. The method according to claim 1 wherein step c) comprises heating the solution to at least 250°C under vigorous stirring for 30 minutes or until the solution clears.
8. The method according to claim 1 wherein the precursor solution is injected into the heated mixture in less than 2 seconds.
9. The method according to claim 1 wherein the precursor solution is injected into the heated mixture in less than 1 second.

10. The method according to claim 1 wherein the injection temperature is between about 220 and 260°C
11. The method according to claim 1 wherein the precursor is Cd.
12. The method according to claim 1 wherein step a) comprises dissolving selenium powder in trioctylphosphine (TOP) (Se/TOP = 1/8 molar ratio).
13. The method according to claim 1, further comprising the step of
 - e) quenching the growth solution.
14. The method according to claim 13 wherein step e) comprises cooling the growth solution to less than 200°C.
15. The method according to claim 13 wherein step e) comprises cooling the growth solution to less than 150°C.
16. The method according to claim 13 wherein step e) comprises cooling the growth solution to less than 120°C.
17. The method according to claim 13, further comprising the step of
 - f) re-heating the quenched growth solution.
18. The method according to claim 17 wherein step e) comprises re-heating the growth solution to at least 120°C.
19. The method according to claim 17 wherein step e) comprises re-heating the growth solution to at least 150°C.

20. The method according to claim 1 wherein the first solvent is selected from the group consisting of Dowtherm G, Dowtherm RP, Dowtherm Q, Dowtherm J, Dowtherm HT, Dowtherm T, and Dowtherm MX.

21. The method according to claim 1 wherein the first solvent is selected from the group consisting of inorganic solvents, silicone oil, related siloxane compounds having a molecular backbone of Si-O-Si bonds, and fluorinated solvents.

22. The method according to claim 1 wherein the first solvent comprises a phenylated compound.

DESCRIPTION OF THE FIGURES

Figure (1) Shows UV-Vis Absorption spectra for the CdSe nanocrystal synthesized in different solvents (Dowtherm A, biphenyl, and phenyl Ether) at 160°C

Figure (2) Fluorescence spectra for the CdSe nanocrystal synthesized in different solvents (Dowtherm A, biphenyl, and phenyl Ether) 160°C

Figure (3) UV-Vis spectra for CdSe quantum dot synthesized in ODE at 100°C shows no significant growth with time

Figure (4) UV-Vis spectra for CdSe nanocrystals synthesized in ODE shows the growth of nanoparticles with time at 160°C

Figure (5) Fluorescence Spectra for CdSe nanocrystals synthesized in ODE shows the growth of nanoparticles with time at 160°C

Figure (6) UV-Vis Spectra for CdSe quantum dot synthesized in Dowtherm A at 100°C shows no significant growth with time

Figure (7) UV-Vis Spectra for CdSe quantum dot synthesized in Dowtherm A at 160°C shows no significant growth with time

Figure (8) Fluorescence Spectra for CdSe quantum dot synthesized in Dowtherm A at 160°C shows no significant growth with time

DESCRIPTION OF TABLES

Table (1) Comparison of the prices of different solvents

Table (2) Comparison of the particle size and particle size distribution for CdSe quantum dot synthesized in different solvents (Dowtherm A, biphenyl, and phenyl Ether)

Table (3) CdSe Quantum dot synthesized in octadecene at 160°C

Table (4) Different types of Dowtherm

REFERENCES

- [1] Alivisatos, A. P., *Science* **271**, 933-937 (1996)
- [2] Murray, C. B., Kagan, C. R., and Bawendi, M. G., *Annual Review of Materials Science* **30**, 545-610 (2000)
- [3] Bukowski, T. J. and Simmons J. H., *Critical Reviews in Solid State and Materials Science* **27**, 119-142 (2002)
- [4] Murray, C. B., Norris, D. J., Bawendi, M. G., *Journal of the American Chemical Society* **115**, 8706-8715 (1993)
- [5] Katari, J. E. B., Colvin, V. L., Alivisatos, A. P., *Journal of Physical Chemistry* **98**, 4109-4117 (1994)
- [6] Dabbousi, B. O., Rodriguez-Viejo, J., Mikulec, F. V., Heine, J. R., Matoussi, H., Ober, R., Jensen, K. F., and Bawendi, M. G., *Journal of Physical Chemistry B* **101**, 9463-9475 (1997)
- [7] Manna, L., Scher, E. C., Alivisatos, P., *Journal of the American Chemical Society* **122**, 12700-12706 (2000)
- [8] Peng, Z. A. and Peng, X., *Journal of the American Chemical Society* **123**, 1389-1395 (2001)
- [9] Peng, X., Wickham, J., Alivisatos, A. P., *Journal of the American Chemical Society* **120**, 5343-5344 (1998)
- [10] Duan, X. and Lieber, C. M., *Advanced Materials* **12**, 298-302 (2000)
- [11] Qu, L., Peng, Z. A., Peng, X., *Nano Letters* **1**, 333-337 (2001)
- [12] Qu, L. and Peng, X., *Journal of the American Chemical Society* **124**, 2049-2055 (2002)
- [13] Wang, Y. A., Li, J. J., Chen, H., Peng, X., *Journal of the American Chemical Society* **124**, 2293-2298 (2002)
- [14] Yu, W. W. and Peng, X., *Angewandte Chemie International Edition* **41**, 2368-2371 (2002)
- [15] <http://www.dow.com/heattrans/family/dowa/index.htm>

Table (1) Comparison of the prices of different solvents

Solvent	Price (\$/kg)	m. p (°C)
TOPO (from ALDRICH)	104	52
ODE (from ALDRICH)	24	18
DT (from Dow Chemicals)	2	12

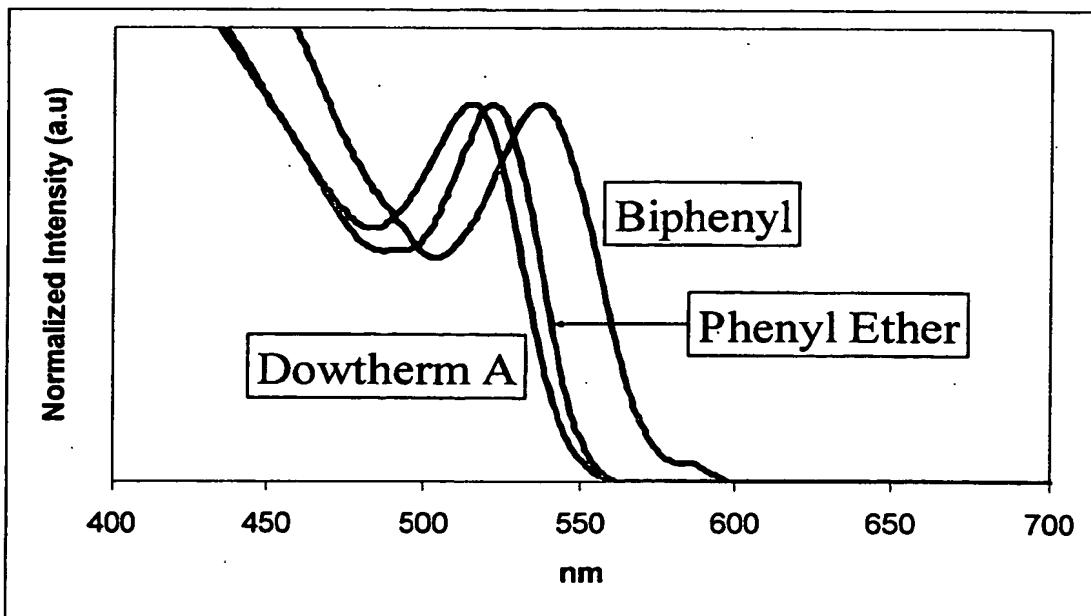


Figure (1) UV-Vis Absorption spectra for the CdSe nanocrystal synthesized in different solvents (Dowtherm A, biphenyl, and phenyl Ether) at 160°C

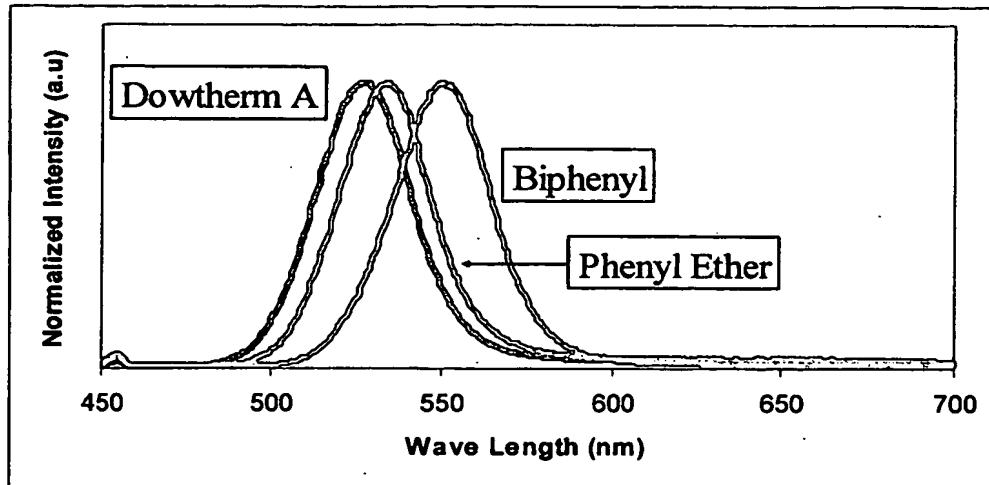


Figure (2) Fluorescence spectra for the CdSe nanocrystal synthesized in different solvents (Dowtherm A, biphenyl, and phenyl Ether) 160°C

Table (2) Comparison of the particle size and particle size distribution for CdSe quantum dots synthesized in different solvents (Dowtherm A, biphenyl, and phenyl ether)

Solvent	FWHM (nm)	Particle Size (nm)
Dowtherm A	32	2.4
Phenyl Ether	31	2.5
Biphenyl	33	2.8

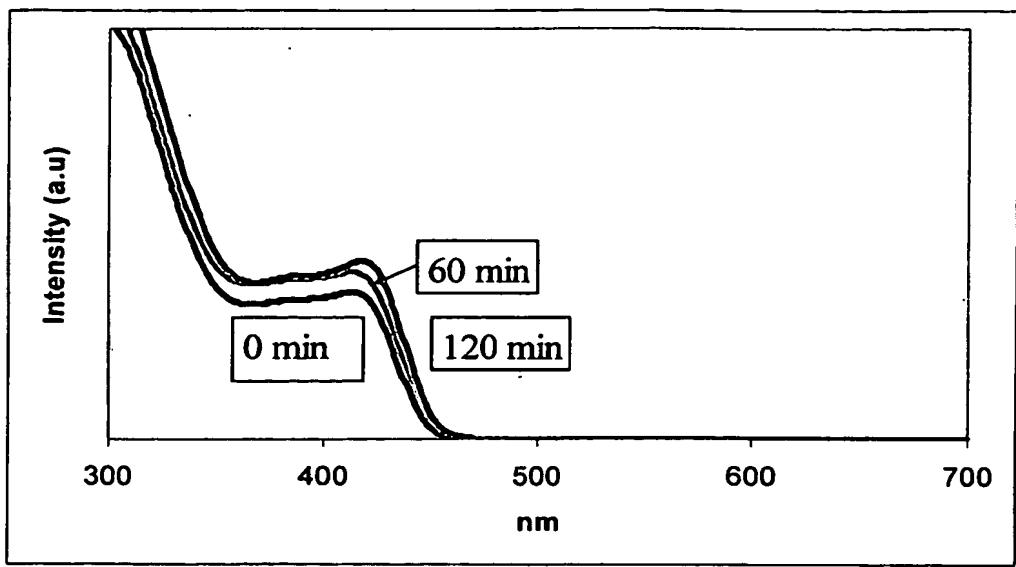


Figure (3) UV-Vis spectra for CdSe quantum dot synthesized in ODE at 100°C shows no significant growth with time

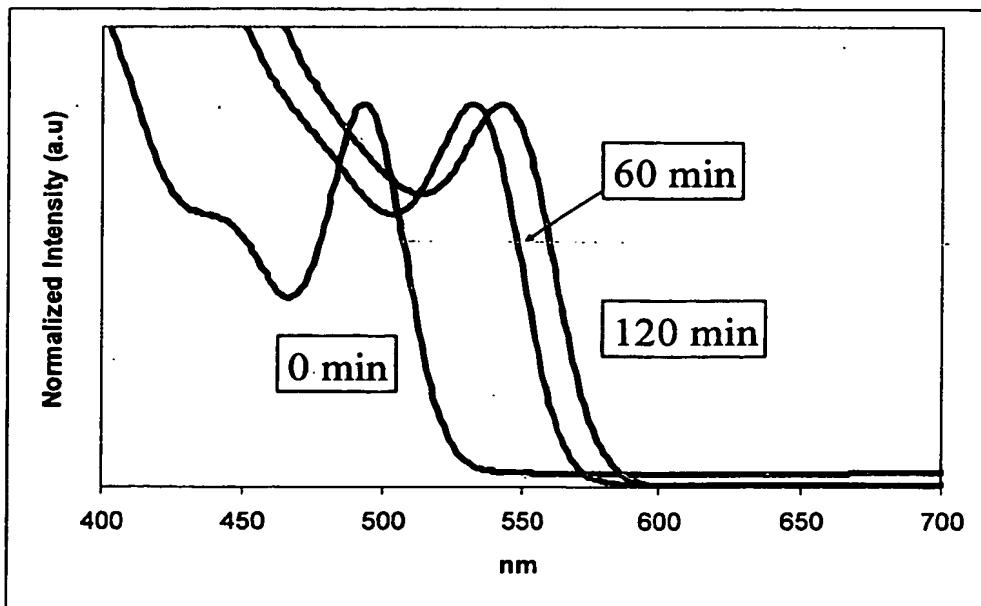


Figure (4) UV-Vis spectra for CdSe nanocrystals synthesized in ODE shows the growth of nanoparticles with time at 160°C

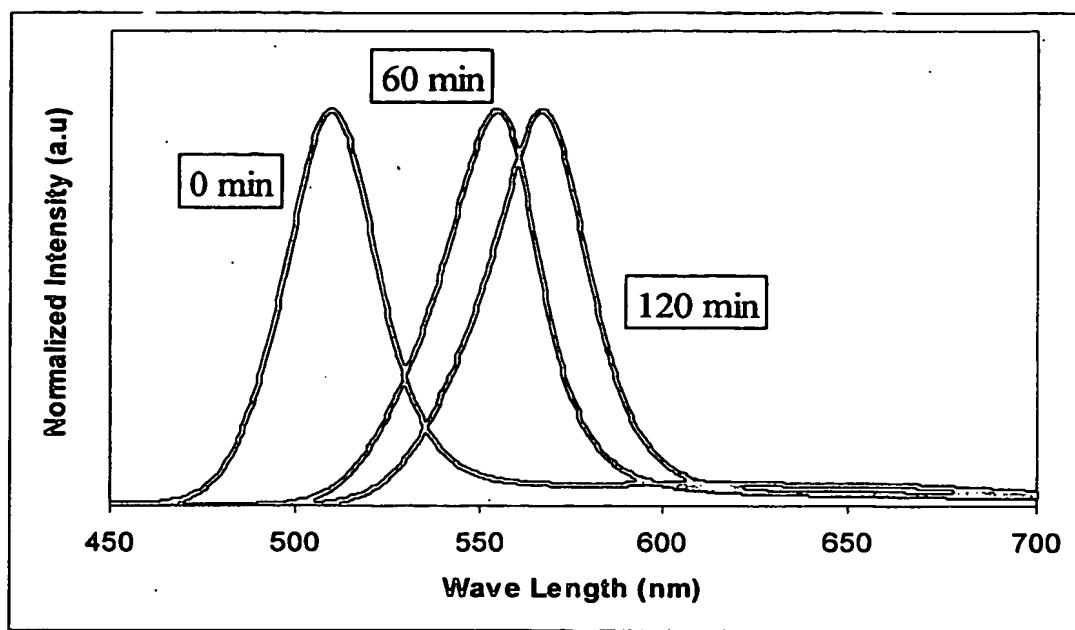


Figure (5) Fluorescence Spectra for CdSe nanocrystals synthesized in ODE shows the growth of nanoparticles with time at 160°C

Table (3) CdSe Quantum dot synthesized in octadecene at 160°C

Time (min)	FWHM	Particle Size (nm)	Product Yield (%)	Total Yield (mg/ml)
0	26.6	2.2	60.2	0.60
10	32.9	2.4	64.4	0.64
30	33.5	2.5	76.5	0.76
60	33.5	2.7	90.5	0.90
90	33.8	2.8	95.4	0.95
120	34.1	2.9	98.5	0.98

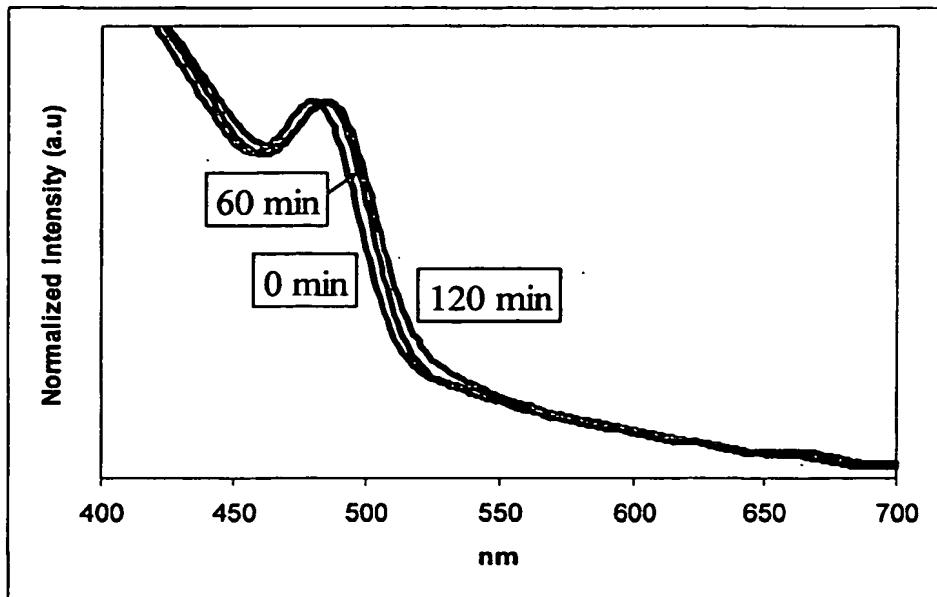


Figure (6) UV-Vis Spectra for CdSe quantum dot synthesized in Dowtherm A at 100°C shows no significant growth with time

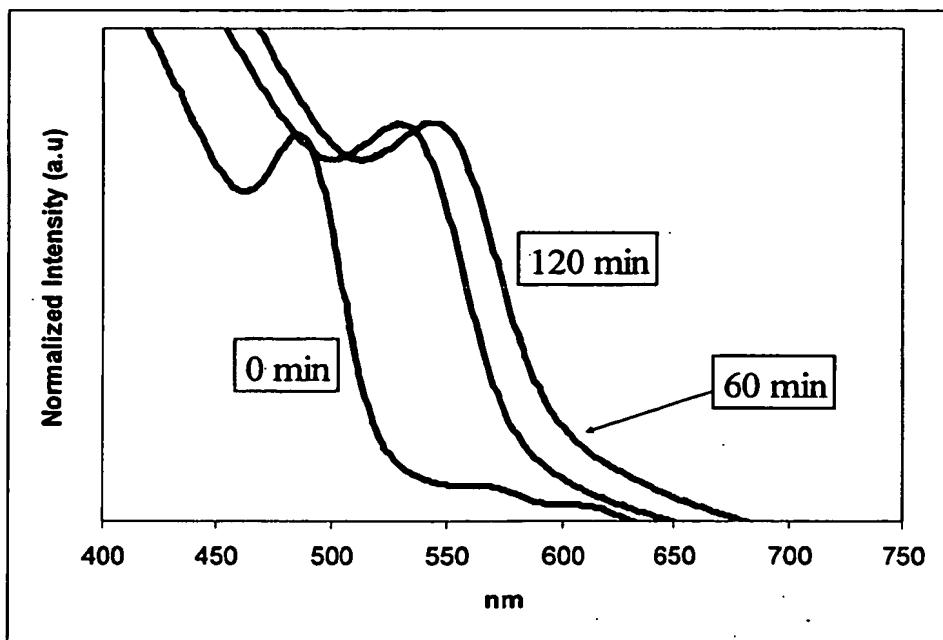


Figure (7) UV-Vis Spectra for CdSe quantum dot synthesized in Dowtherm A at 160°C shows no significant growth with time

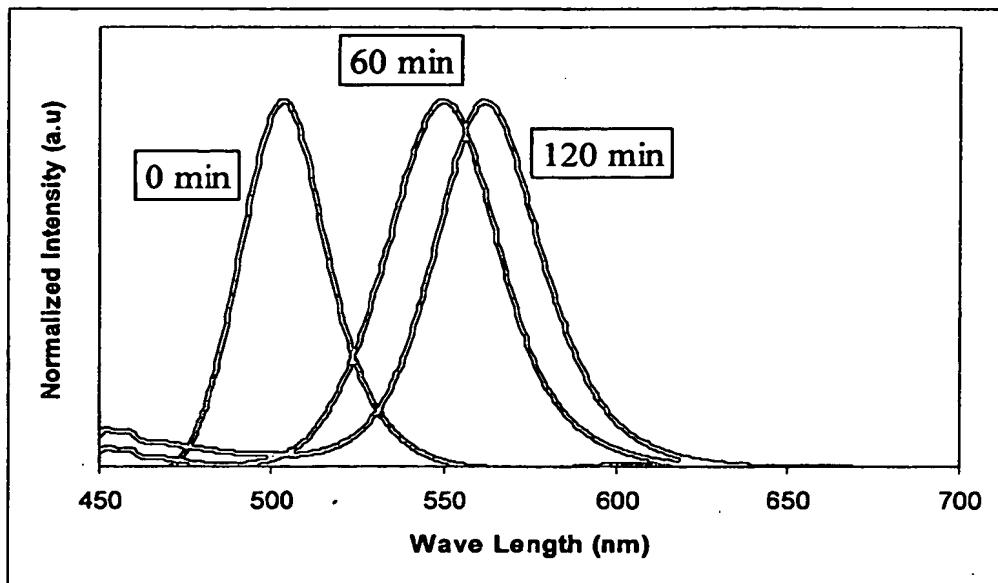


Figure (8) Fluorescence Spectra for CdSe quantum dot synthesized in Dowtherm A at 160°C shows no significant growth with time

Table (4) Different types of Dowtherm

Solvent	Composition	Melting point (°C)	Boiling point (°C)
Dowtherm G	di-/tri- aryl ethers	4	288
Dowtherm RP	diaryl alkyl		353
Dowtherm Q	diphenylethane and alkylated aromatics		267
Dowtherm J	isomers of an alkylated aromatic	< -81	181
Dowtherm HT	modified terphenyl fluid		345
Dowtherm T	C ₁₄ -C ₃₀ alkyl benzenes		210
Dowtherm MX	alkylated aromatics		328

ABSTRACT

New solvents and method for the synthesis of quantum dot are disclosed. Dowtherm A; a low-priced commercially available heating fluid is used as a solvent to synthesize CdSe nanocrystals. Moreover, phenyl ether and biphenyl are also used for the same purpose.

Separation between nucleation and growth is achieved by quenching the reaction solution with the appropriate amount of cold solvent (room temperature) to lower the temperature to the level where the reaction stops, followed by raising the temperature to the desired level to allow growth to take place.



DOWTHERM A

Synthetic Organic Heat Transfer Fluid—Liquid and Vapor Phase Data

DOWTHERM® A heat transfer fluid is a eutectic mixture of two very stable compounds, biphenyl ($C_{12}H_{10}$) and diphenyl oxide ($C_{12}H_{10}O$). These compounds have practically the same vapor pressures, so the mixture can be handled as if it were a single compound. DOWTHERM A fluid may be used in systems employing either liquid phase or vapor phase heating.

Recommended use temperature range:

Liquid phase: 15°C (60°F) to 400°C (750°F)

Vapor phase: 257°C (495°F) to 400°C (750°F)

Suitable applications: Indirect heat transfer

For health and safety information for this product, contact your Dow sales representative or call the number for your area on the second page of this sheet for a Material Safety Data Sheet (MSDS).

Typical Properties of DOWTHERM A Fluid†

Composition: Diphenyl Oxide/Biphenyl Blend

Color: Clear to Light Yellow

Property	SI Units	English Units
Freeze Point	12.0°C	53.6°F
Atmospheric Boiling Point	257.1°C	494.8°F
Flash Point ¹	113°C	236°F
Fire Point ²	118°C	245°F
Autoignition Temperature ³	599°C	1110°F
Density @ 25°C (75°F)	1056 kg/m^3	66.0 lb/ft^3
Surface Tension in Air @		
20°C (68°F)	40.1 Dynes/cm	40.1 Dynes/cm
40°C (104°F)	37.6 Dynes/cm	37.6 Dynes/cm
60°C (140°F)	35.7 Dynes/cm	35.7 Dynes/cm
Estimated Critical Temperature	497°C	927°F
Estimated Critical Pressure	31.34 bar	30.93 atm
Estimated Critical Volume	3.17 l/kg	0.0508 ft ³ /lb
Average Molecular Weight		166.0
Heat of Combustion	36,053 kJ/kg	15,500 Btu/lb

¹ Not to be construed as specifications

² SETA

³ C.O.C.

⁴ ASTM E659-78

Saturated Liquid Properties of DOWTHERM A Fluid (SI units)

Temp. °C	Vapor Pressure bar	Viscosity mPa sec	Specific Heat kJ/kg K	Thermal Cond. W/mK	Density kg/m ³
15	0.00	5.00	1.558	0.1395	1063.5
65	0.00	1.58	1.701	0.1315	1023.7
105	0.01	0.91	1.814	0.1251	990.7
155	0.06	0.56	1.954	0.1171	947.8
205	0.28	0.38	2.093	0.1091	902.5
255	0.97	0.27	2.231	0.1011	854.0
305	2.60	0.20	2.373	0.0931	801.3
355	5.80	0.16	2.527	0.0851	742.3
405	11.32	0.12	2.725	0.0771	672.5

Saturated Liquid Properties of DOWTHERM A Fluid (English units)

Temp. °F	Vapor Pressure psia	Viscosity cP	Specific Heat Btu/lb °F	Thermal Cond. Btu/hr ft ² (°F/R)	Density lb/ft ³
60	0.000	4.91	0.373	0.0805	66.37
120	0.003	2.12	0.396	0.0775	64.72
180	0.028	1.22	0.418	0.0744	63.03
240	0.16	0.81	0.441	0.0713	61.30
300	0.64	0.59	0.463	0.0682	59.51
360	2.03	0.45	0.485	0.0651	57.65
420	5.38	0.35	0.507	0.0620	55.72
480	12.25	0.28	0.529	0.0590	53.70
540	24.72	0.23	0.552	0.0559	51.57
600	45.31	0.19	0.575	0.0528	49.29
660	76.89	0.16	0.599	0.0497	46.82
720	122.7	0.14	0.627	0.0466	44.08
780	186.4	0.12	0.665	0.0436	40.93

DOWTHERM A Synthetic Organic Heat Transfer Fluid

Saturated Vapor Properties of DOWTHERM A Fluid (SI Units)

Temp. °C	Vapor Pressure bar	Liquid Enthalpy kJ/kg	Latent Heat kJ/kg	Vapor Enthalpy kJ/kg	Vapor Density kg/m³	Vapor Viscosity mPa·s	Vapor Thermal Cond. W/mK	Z_{vapor}	Specific Heat (c_p) kJ/kg K	Ratio of Specific Heats c_p/c_v
15	0.00	4.9	407.2	412.1		0.0054	0.0075	1.000	1.044	1.050
65	0.00	88.1	380.9	469.1	0.0040	0.0063	0.0104	1.000	1.227	1.043
105	0.01	158.1	362.7	520.9	0.0341	0.0071	0.0129	0.999	1.366	1.038
155	0.06	251.2	341.5	592.7	0.2583	0.0080	0.0163	0.995	1.528	1.035
205	0.28	351.2	320.2	671.5	1.179	0.0090	0.0200	0.982	1.681	1.034
255	0.97	458.2	297.4	755.6	3.831	0.0100	0.0238	0.954	1.829	1.036
305	2.60	572.2	271.5	843.6	9.896	0.0110	0.0279	0.908	1.976	1.042
355	5.80	693.1	240.6	933.8	22.03	0.0122	0.0322	0.838	2.133	1.057
405	11.32	822.0	201.7	1023.7	45.17	0.0138	0.0368	0.740	2.333	1.094

Saturated Vapor Properties of DOWTHERM A Fluid (English Units)

Temp. °F	Vapor Pressure psia	Liquid Enthalpy Btu/lb	Latent Heat Btu/lb	Vapor Enthalpy Btu/lb	Vapor Density lb/ft³	Vapor Viscosity cP	Vapor Thermal Cond. Btu/hr ft²(°F/ft)	Z_{vapor}	Specific Heat (c_p) Btu/lb °F	Ratio of Specific Heats c_p/c_v
60	0.000	2.5	175.1	177.6		0.0054	0.0044	1.000	0.250	1.050
120	0.003	26.2	167.3	193.5		0.0060	0.0055	1.000	0.279	1.045
300	0.64	103.0	148.0	251.1	0.0130	0.0079	0.0092	0.996	0.361	1.035
360	2.03	131.1	142.0	273.1	0.0388	0.0086	0.0106	0.989	0.385	1.034
420	5.38	160.6	135.8	296.3	0.0967	0.0092	0.0120	0.977	0.409	1.034
480	12.25	191.4	129.2	320.5	0.2100	0.0098	0.0135	0.959	0.433	1.035
540	24.72	223.5	122.1	345.5	0.4102	0.0105	0.0150	0.932	0.456	1.039
600	45.31	256.9	114.2	371.1	0.7389	0.0113	0.0166	0.895	0.480	1.045
660	76.89	291.7	105.3	397.0	1.254	0.0121	0.0183	0.848	0.505	1.055
720	122.7	327.9	95.0	422.9	2.045	0.0130	0.0200	0.789	0.534	1.073
780	186.4	365.9	82.5	448.4	3.270	0.0142	0.0219	0.714	0.571	1.108

For further information, call...

In the United States and Canada: 1-800-447-4369 • FAX: 1-989-832-1465

In Europe: +32 3 450 2240 • FAX: +32 3 450 2815

In the Pacific: +886 22 547 8731 • FAX: +886 22 713 0092

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Nanomanufacturing: Scaling Up Liquid-Phase Production of Optically-Active Nanoparticles

Ammar Alkhawaldeh¹, K. Ausman², V. L. Colvin²,
N. V. Mantzaris¹, M. Pasquali¹, K. Zygourakis¹, and
Michael S. Wong¹

1. Department of Chemical Engineering, 2. Department of Chemistry
Rice University, Houston, TX 77251-1892

Outline

- Introduction
- Large Batch Reactor
- Quenching Method
- New Solvents for Quantum Dot Synthesis
- Conclusions

Objectives

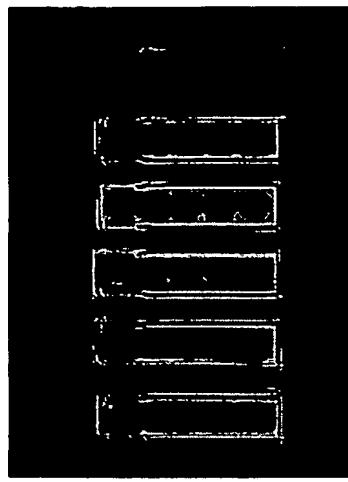
Develop a general methodology for large-scale liquid-phase production of high-quality optically-active nanoparticles:

- Synthesize high-quality quantum dots in a large batch reactor
- Separate nucleation step from growth process
- Use new solvents for the synthesis of quantum dots (QDs)
- Investigate and collect reproducible particle growth data

Quantum Dots

■ *Inorganic nanocrystals luminesce upon UV-vis irradiation:*

- Semiconductor compositions
- Particle sizes of 1-10 nm



■ *Unique characteristics:*

- Photoluminescence (PL) can be finely tuned by particle size
- PL spectral bandwidth is narrow
- Greater photostability compared to organic dyes

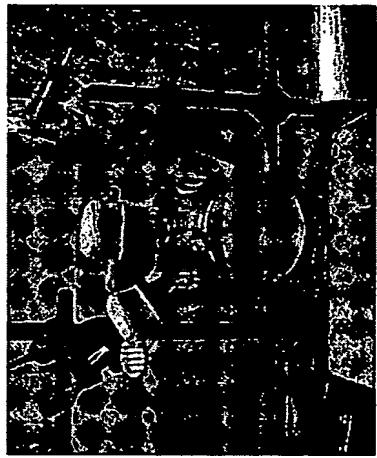
QD particle size

(Dabbousi *et al.*, *J. Phys. Chem. B*, 101, 1997)

■ *High quality:*

- High quantum yield
- Monodisperse

Current Preparation Methods



Before Injection



After Injection

Cadmium Sources:

- $\text{Cd}(\text{CH}_3)_2$ (Hazardous properties)
- $\text{Cd}(\text{Ac})_2$
- CdO

Problems:

- Small quantities
- Difficult to scale up
- Temperature control
- Multiple identical vessels:
 - Batch-to-batch variation
 - Labor intensive
 - High capital cost

Solvents:

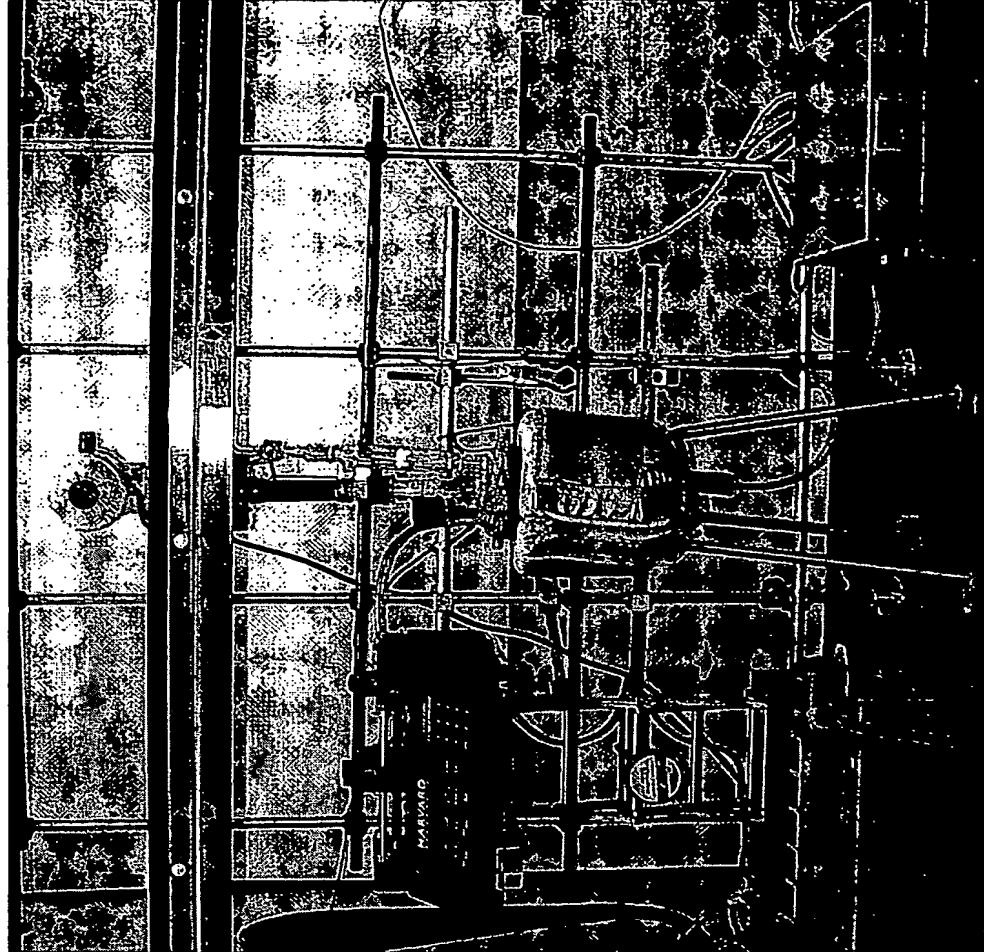
- Trioctylphosphine oxide (TOPO)
- Octadecene (ODE)

Outline

- Introduction
- Large Batch Reactor
- Quenching Method
- New Solvents for Quantum Dot Synthesis
- Conclusions

Our Approach

- 1 L batch reactor



- Automated injection

- New solvents

- Separation of nucleation
and growth

- In situ monitoring
for particle growth
(to be installed)

Materials

(Based on Yu and Peng, *Angew. Chem. Int. Ed.* 41, 2002)

Chemicals:

- Oleic Acid (OA): $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
- Octadecene (ODE): $\text{CH}_3(\text{CH}_2)_{15}\text{CH}=\text{CH}_2$
- Trioctylphosphine (TOP): $[\text{CH}_3(\text{CH}_2)_7]_3\text{P}$
- Cadmium Oxide: CdO
- Selenium Powder: Se

Molar Ratios:

- Cd/Se = 2/1
- Se/TOP = 1/8
- Cd/OA = 1/3
- Cd/ODE = 1/160

Procedure

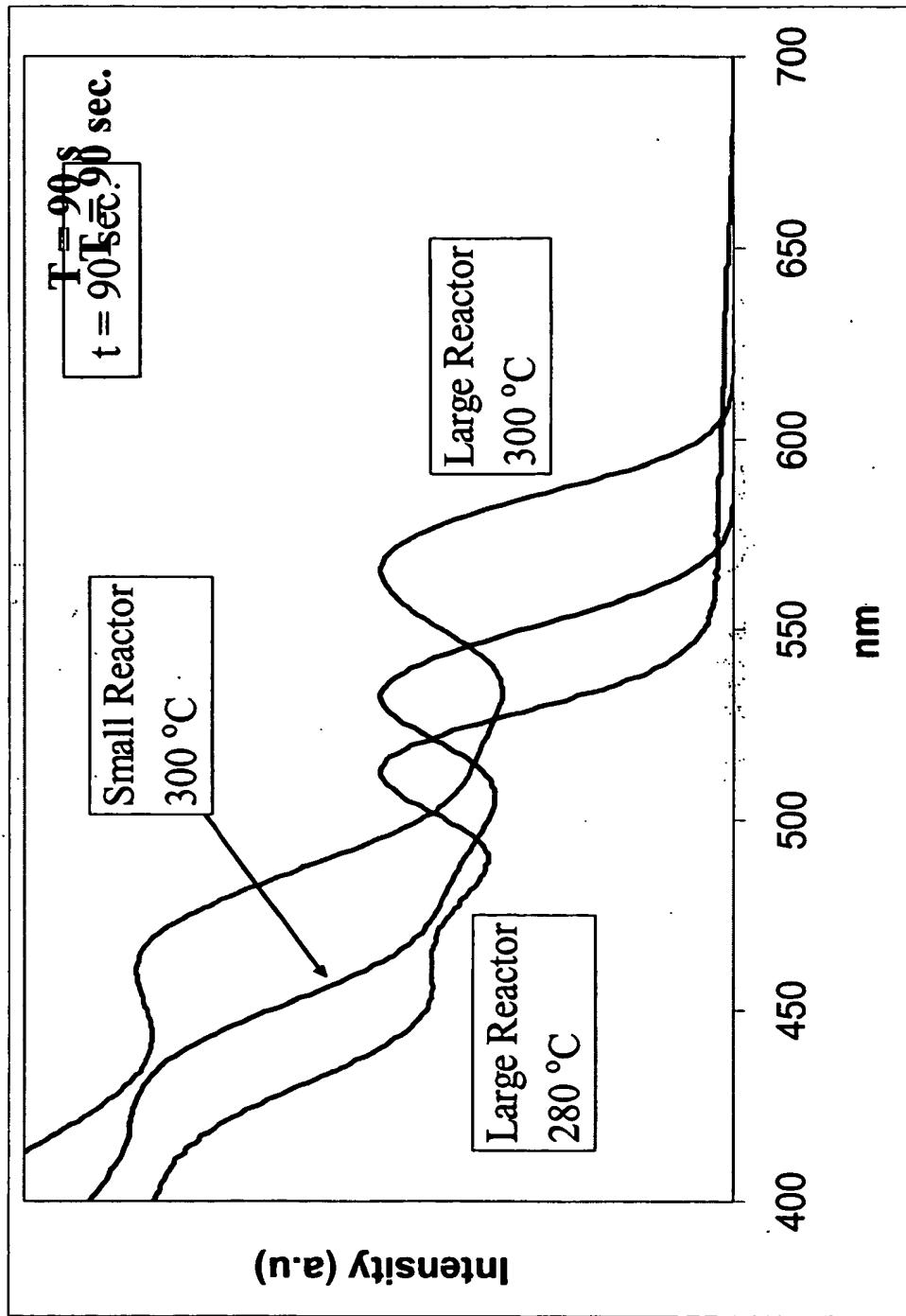
(Based on Yu and Peng, *Angew. Chem. Int. Ed.* 41, 2002)

■ Procedure:

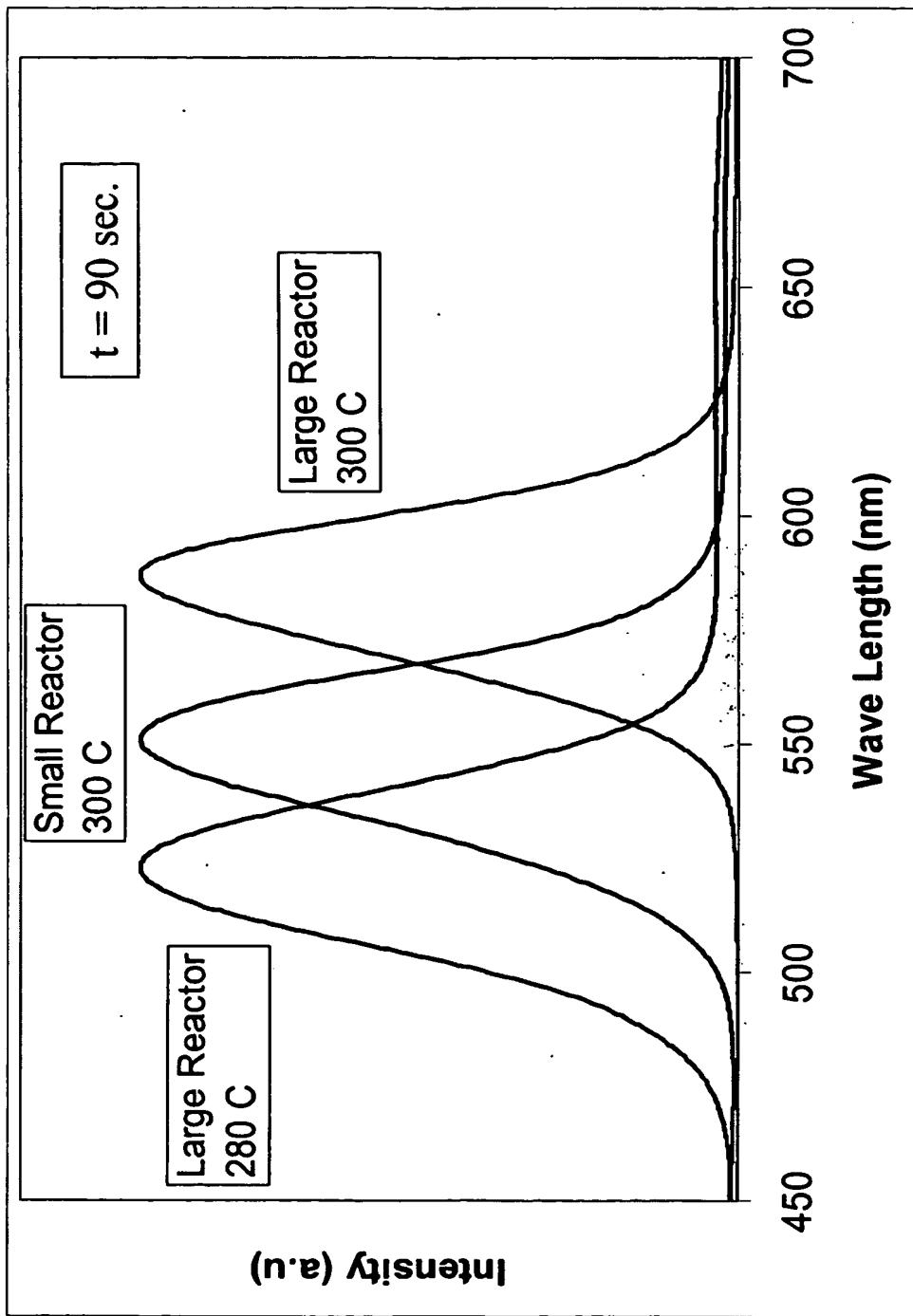
- Prepare the TOPSe solution
- Heat CdO, OA, and ODE to 270 oC or above (Solution will clear up at 260-270 oC)
- Inject the TOPSe at the desired temperature

The diagram illustrates the experimental setup for the synthesis of TOPSe. It features a central reactor vessel surrounded by a heating mantle. A pump is used to circulate the reaction mixture through the system. The reactor is monitored by three thermocouples: one positioned at the top, one on the side, and one at the bottom. The side thermocouple is specifically calibrated to measure the temperatures of CdO, OA, and ODE. The reactor is connected to a 'TOPSe Solution' container, which is part of a larger circuit involving a mixing vessel. The entire assembly is controlled by a 'Temperature Controller' unit.

UV-Vis Spectra for QD in Different Size Reactors



Fluorescence Spectra for QD in Different Size Reactors



Comparison of QD Synthesis in Different Size Reactors

Reactor	FWHM (nm)	Particle Size (nm)	Q. Y. (%)	[QD] mol/l	Product Yield (%)	Total Yield (mg/ml)
Small (300 °C)	36.7	3.1	25	0.01049	97.4	2
Large (300 °C)	35.3	3.4	18	0.01017	96.4	1.95
Large (280 °C)	36.9	2.4	18	0.00490	62.8	0.94

Outline

- Introduction
- Large Batch Reactor
- Quenching Method
- New Solvents for Quantum Dot Synthesis
- Conclusions

Quenching Method

Quenching the reaction solution with cold solvent to stop nucleation and control the growth temperature (separate nucleation from growth)

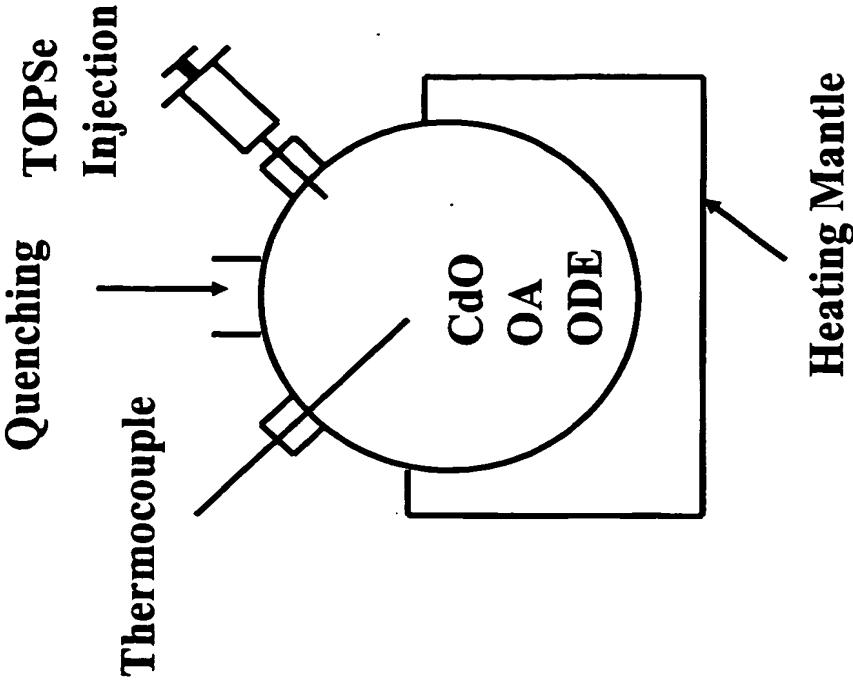
- Quench to 100 °C and maintain for 2 hours
- Quench to 100 °C and raise temperature to the desired level (i.e. 160 °C) and maintain for 2 hours

Procedure

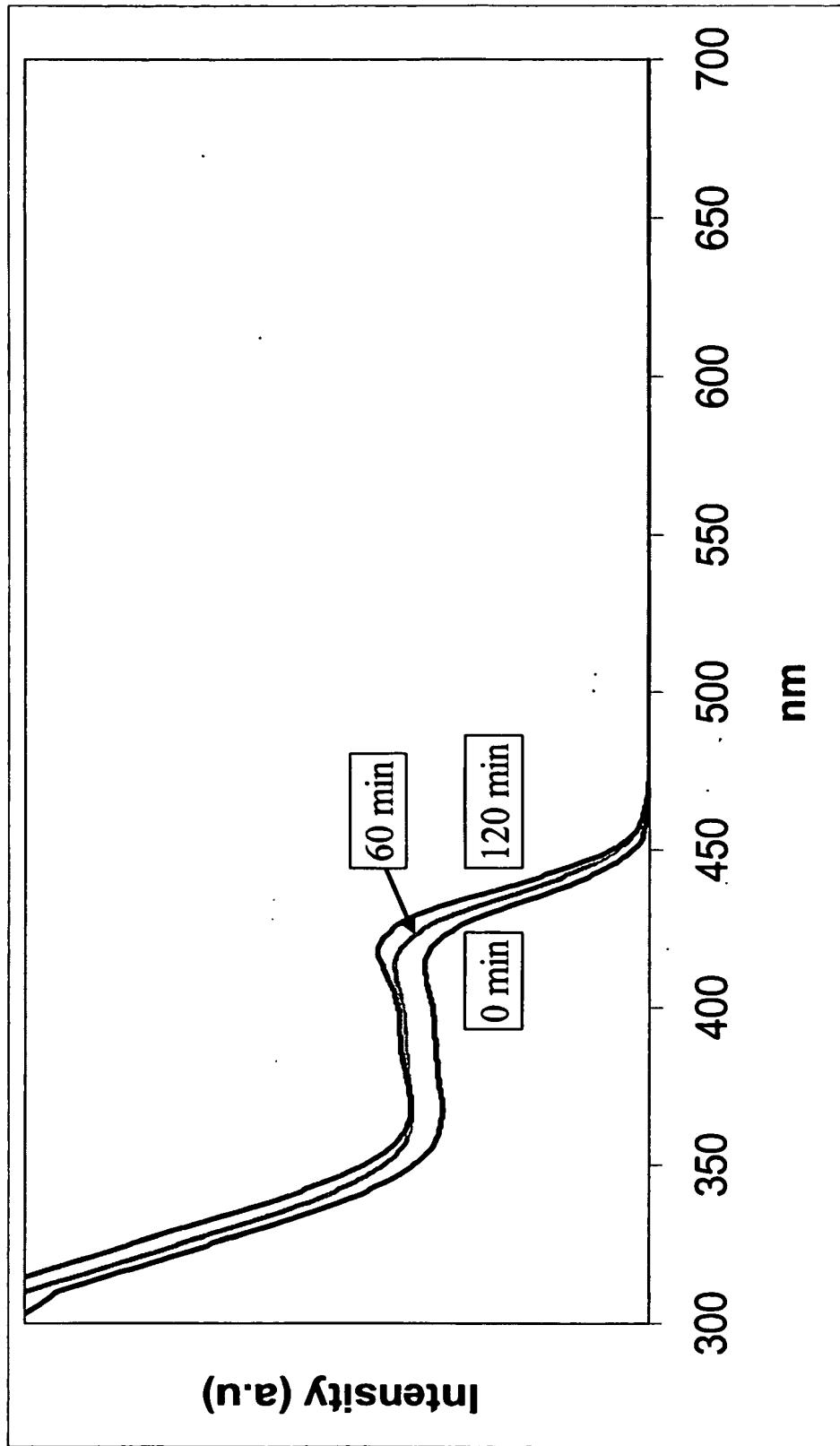
(Based on Yu and Peng, *Angew. Chem. Int. Ed.* 41, 2002)

Procedure:

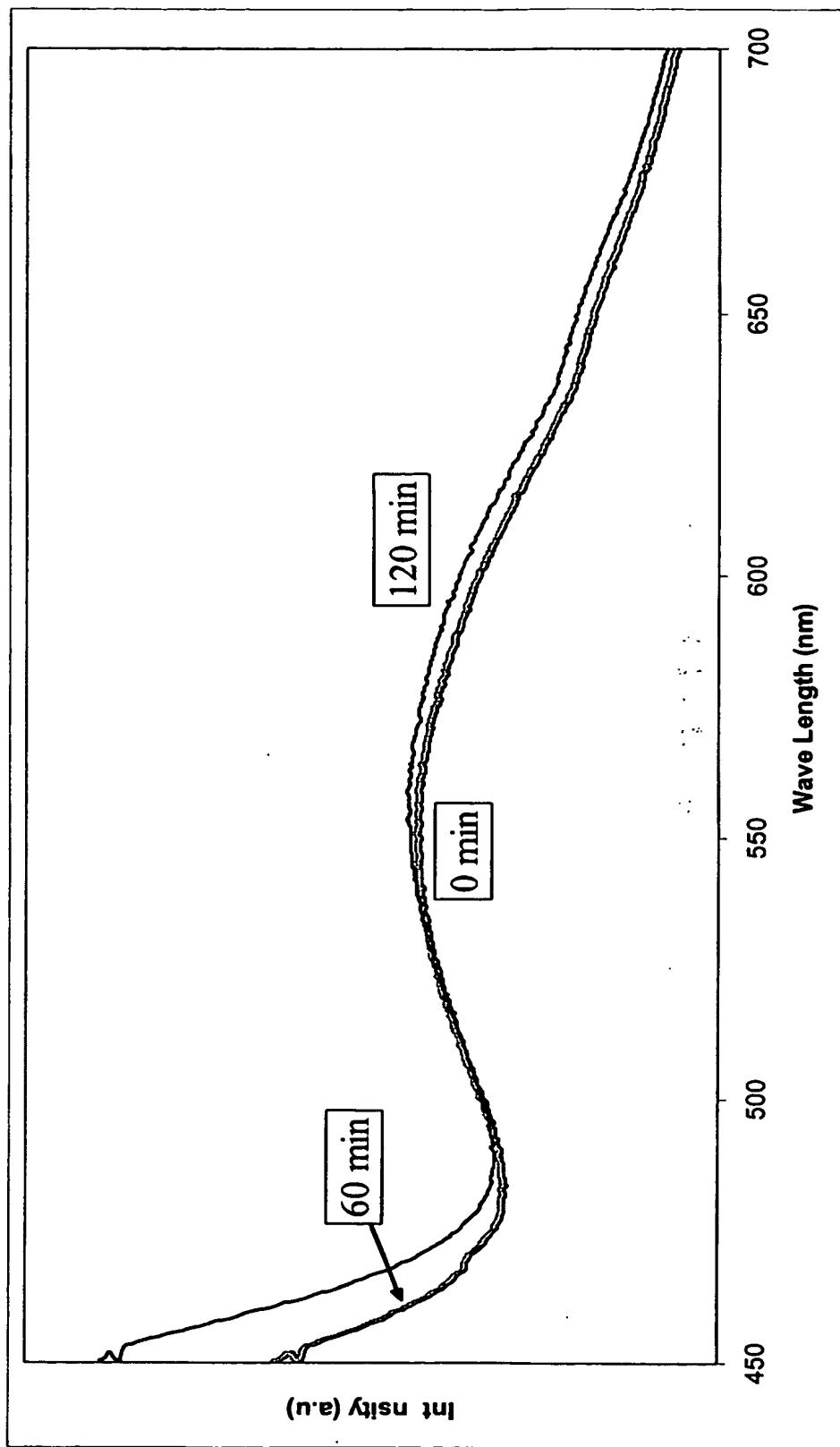
- Prepare the TOPSe solution
- Heat CdO, OA, and ODE to 270 °C or above (Solution will clear up at 260-270 °C)
- Inject the TOPSe at the desired temperature
- Immediately add appropriate amount of cold solvent
- Temperature will drop to 100 °C
- Raise temperature to the desired level



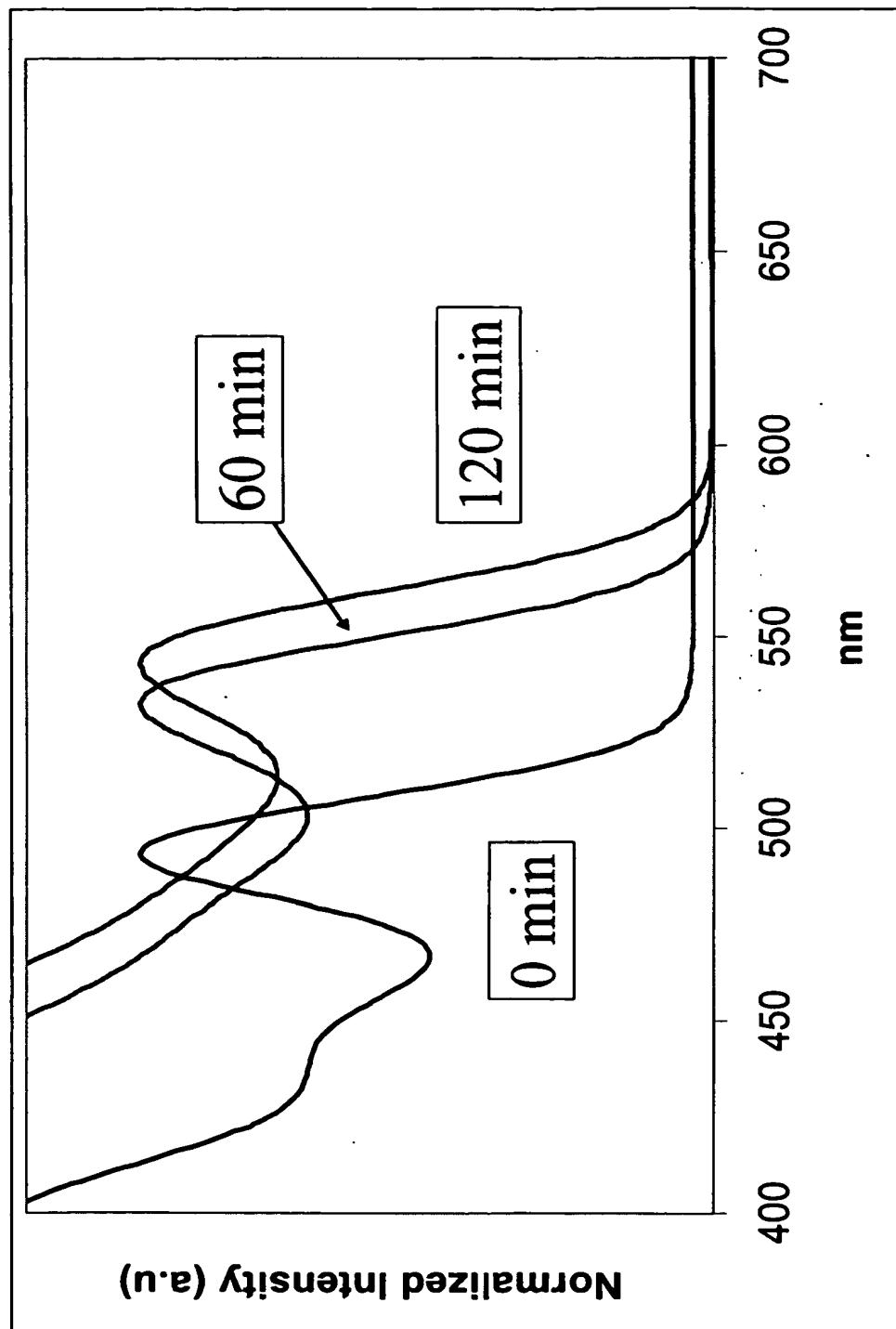
UV-Vis Spectra for CdSe QD in ODE at 100 °C



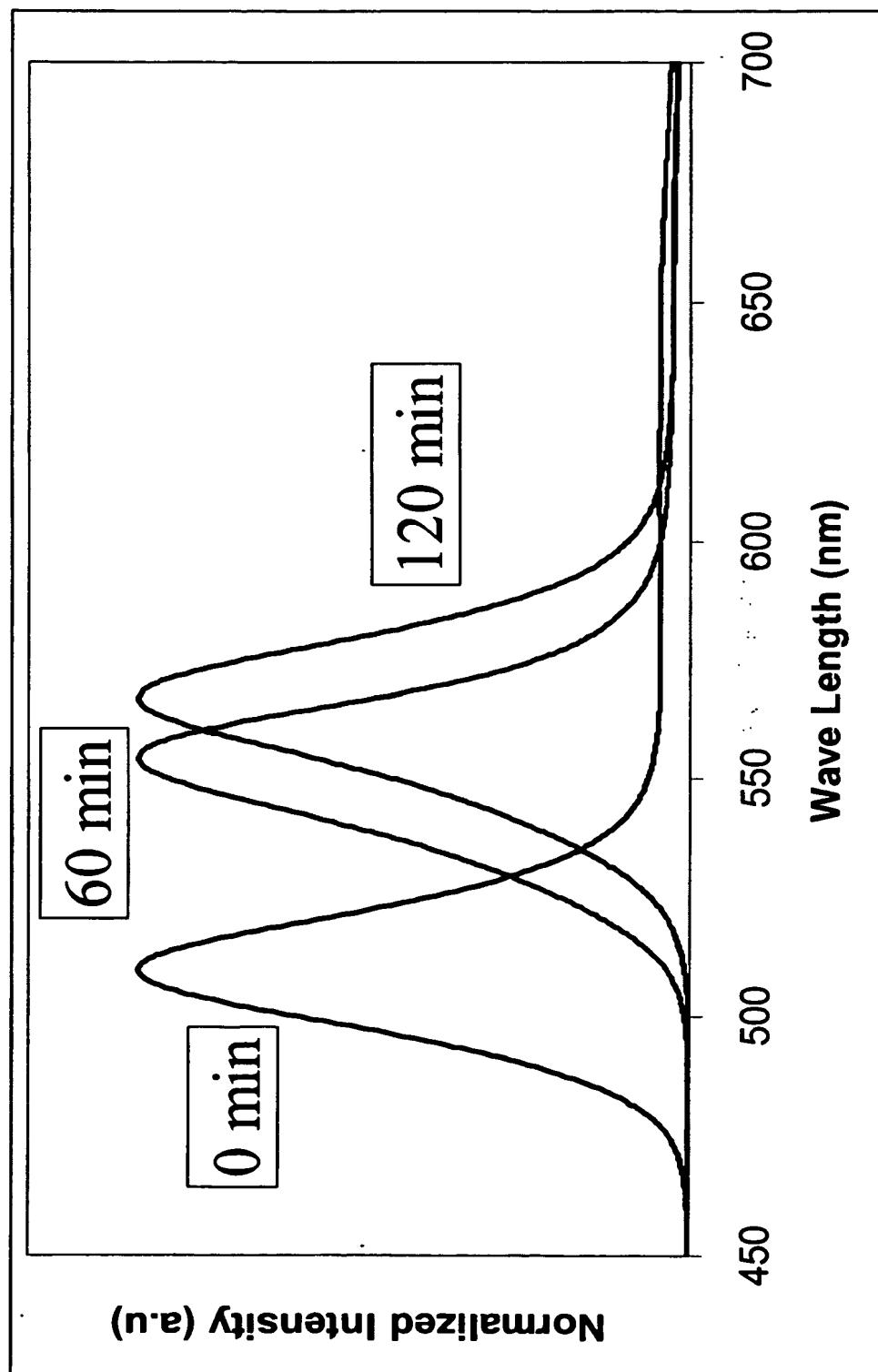
Fluorescence Spectra for QD in ODE at 100 °C



UV-Vis Spectra for QD in ODE at 160 °C



Fluorescence Spectra for QD in ODE at 160 °C



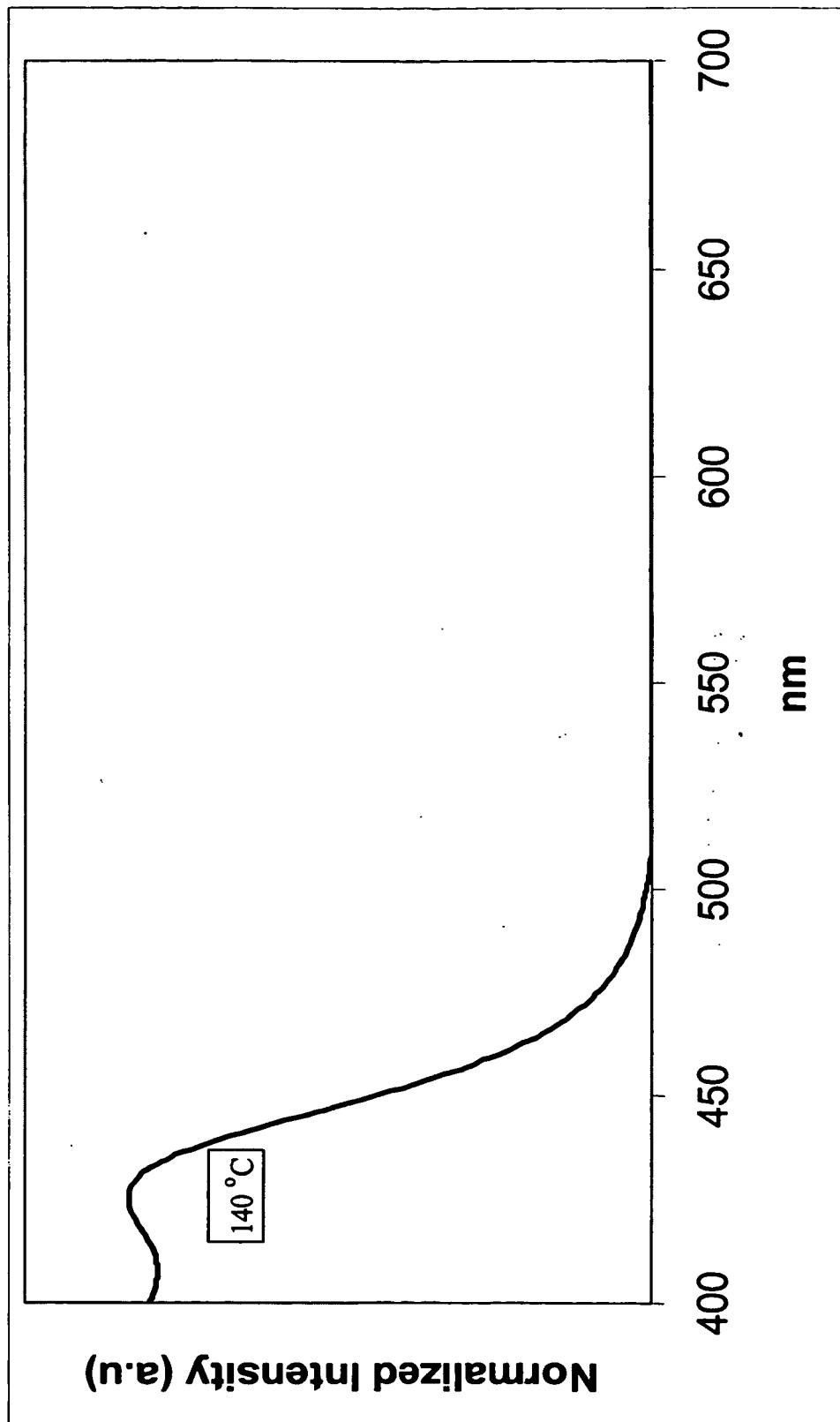
4.

QD Growth in ODE with Time at 160 °C

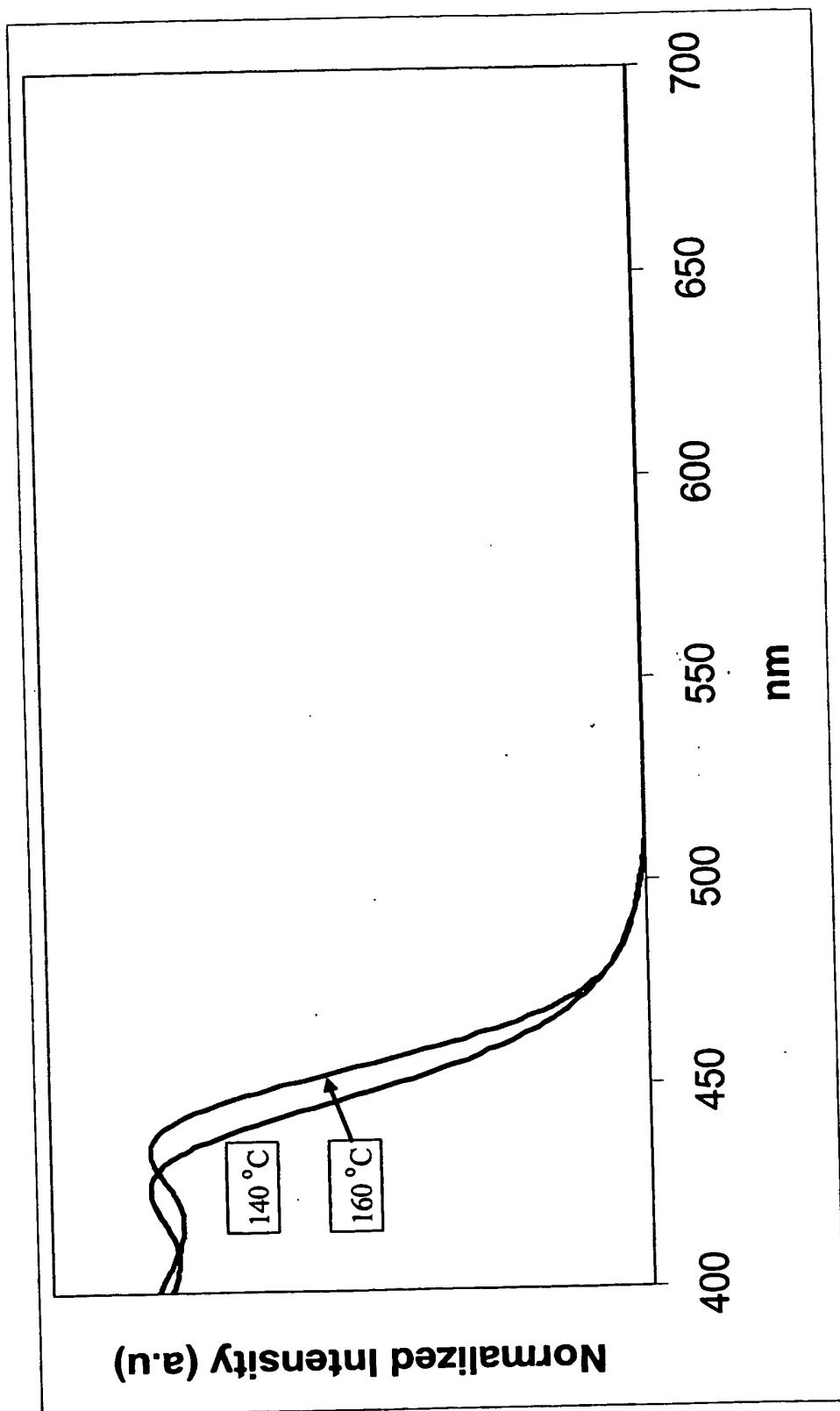
Time (min)	FWHM (nm)	Particle Size (nm)	[QD] mol/l	Product Yield (%)	Total Yield (mg/ml)
0	26.6	2.2	0.003129	60.2	0.60
10	32.9	2.4	0.003344	64.4	0.64
30	33.5	2.5	0.003974	76.5	0.76
60	33.5	2.7	0.004701	90.5	0.90
90	33.8	2.8	0.004954	95.4	0.95
120	34.1	2.9	0.005116	98.5	0.98

N

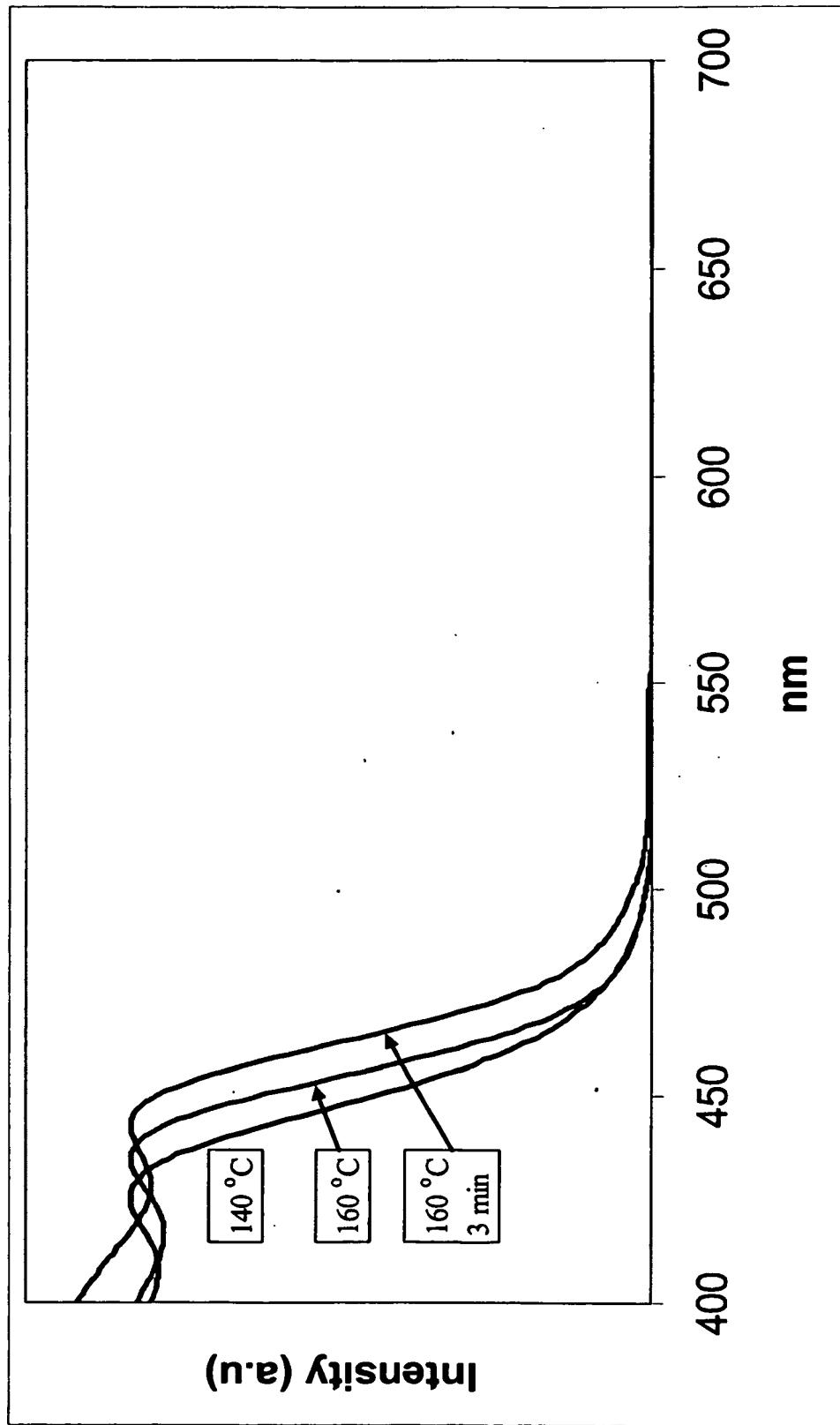
UV-Vis Spectra for QD in ODE



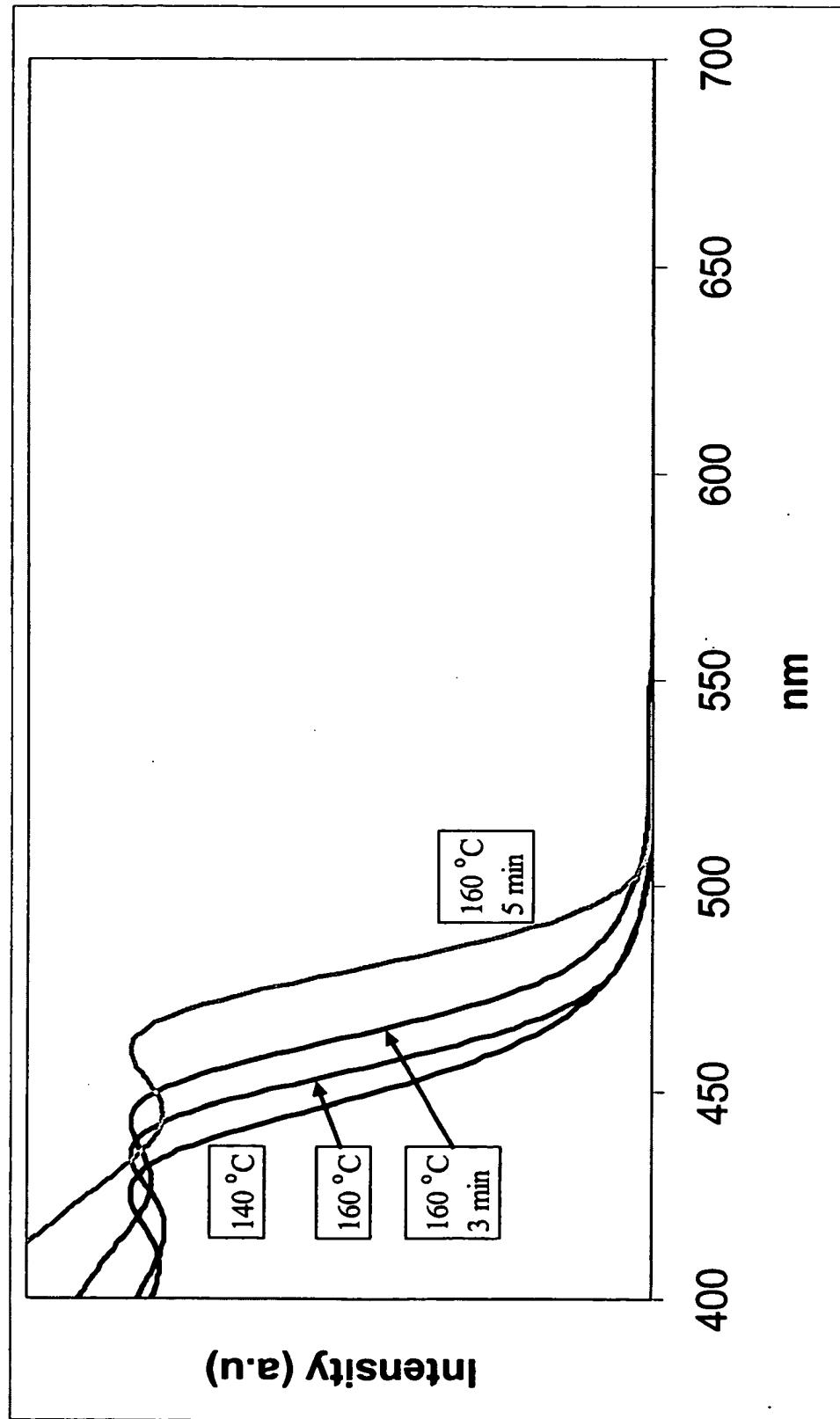
UV-Vis Spectra for QD in ODE



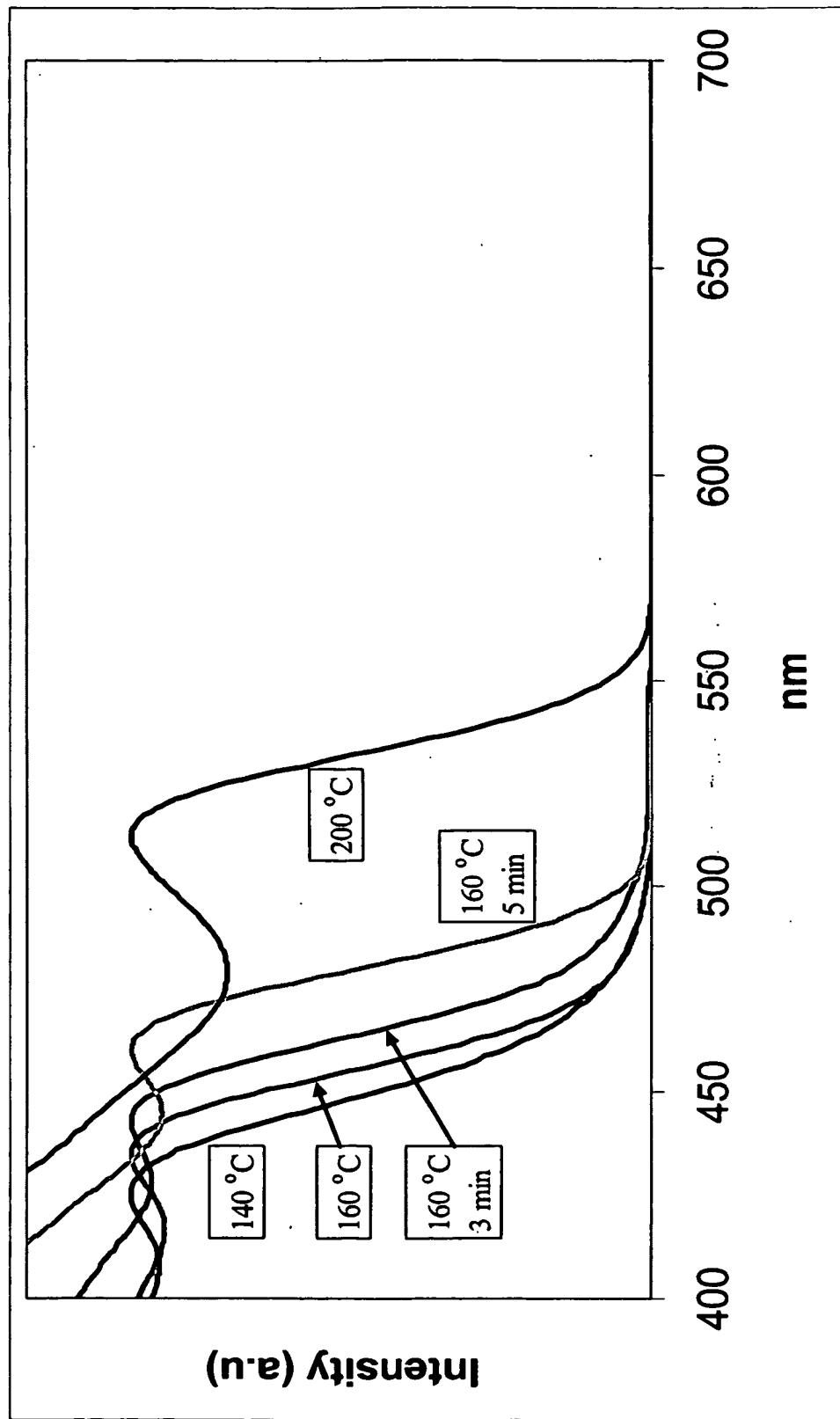
UV-Vis Spectra for QD in ODE



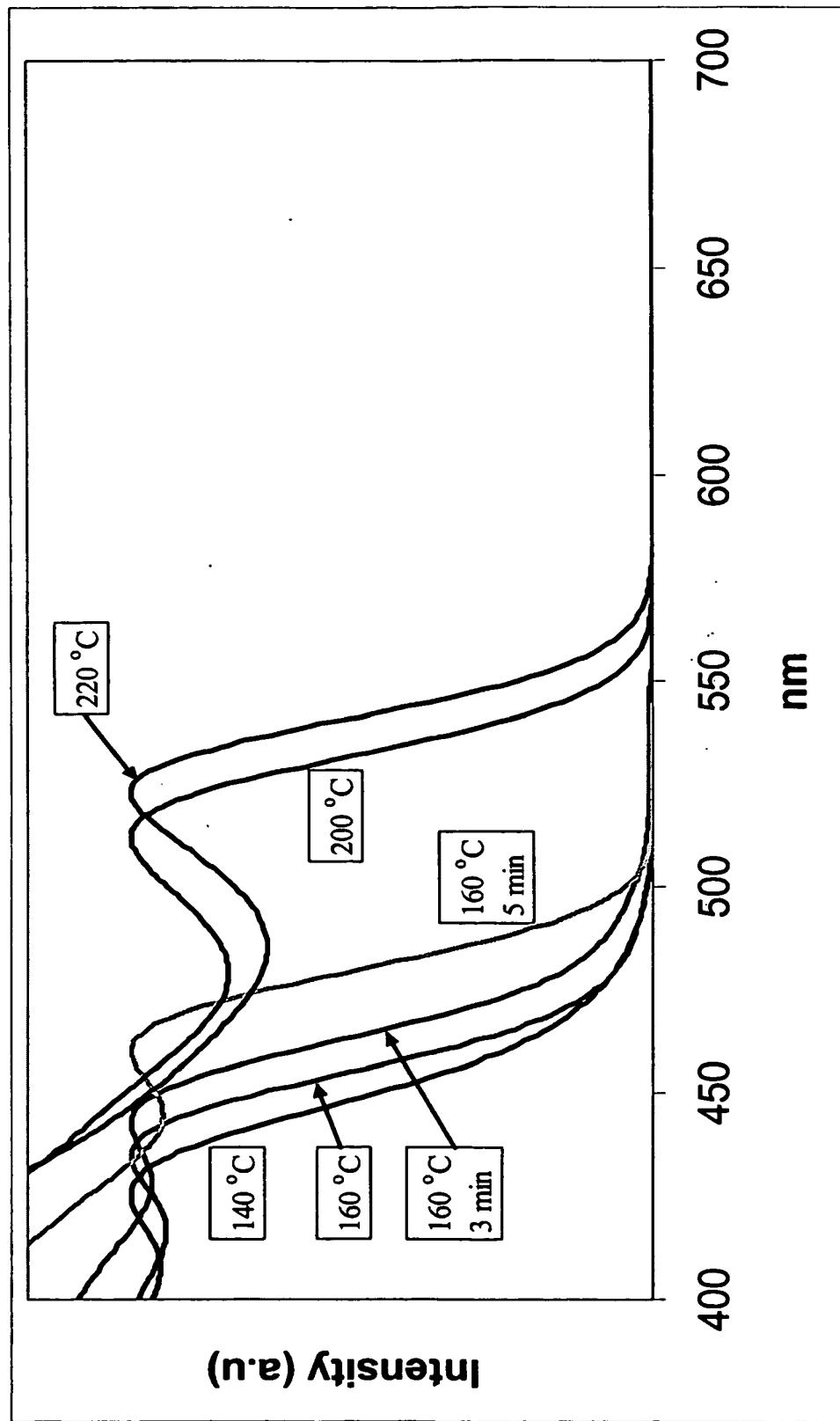
UV-Vis Spectra for QD in ODE



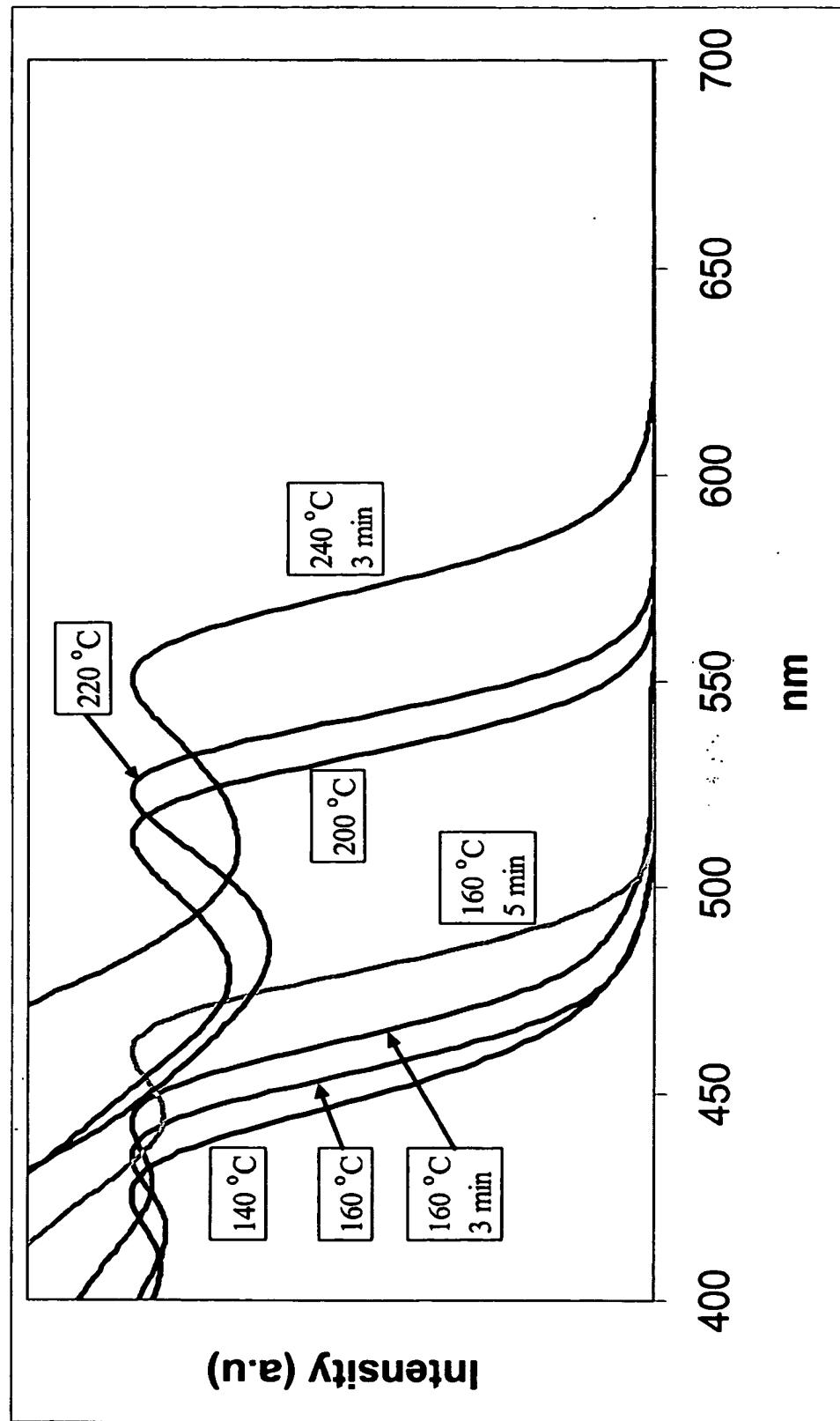
UV-Vis Spectra for QD in ODE



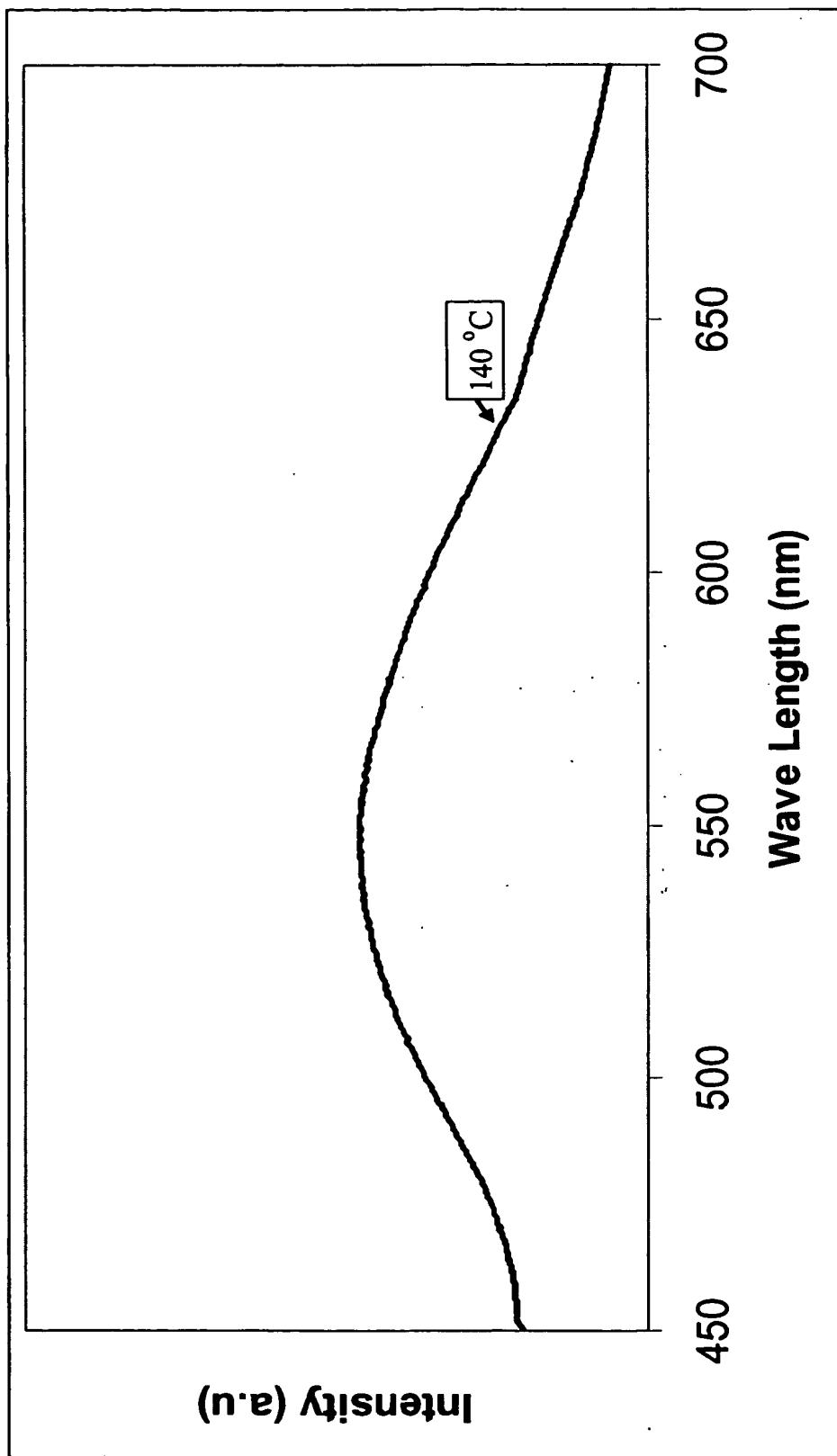
UV-Vis Spectra for QD in ODE



UV-Vis Spectra for QD in ODE

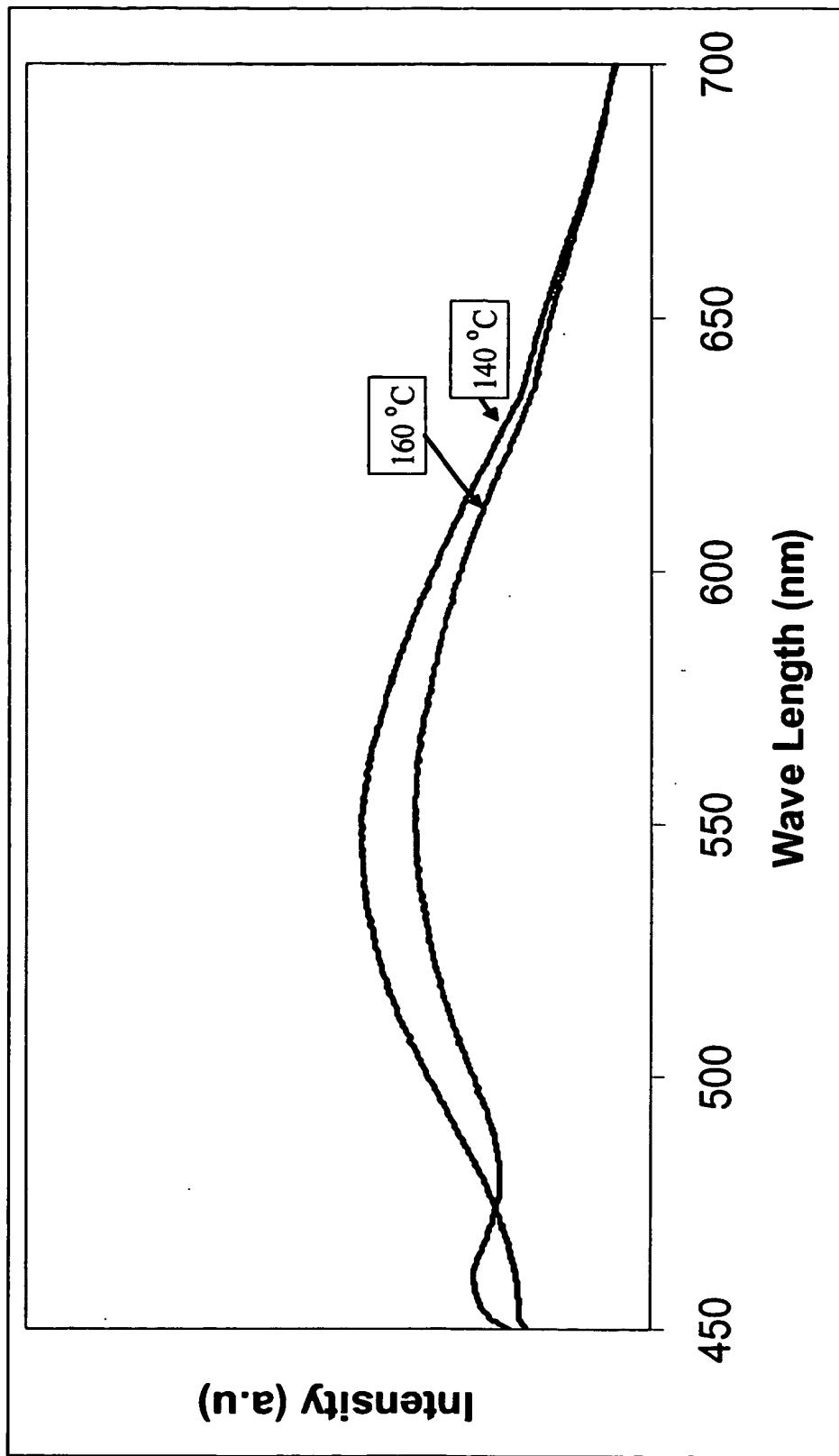


Fluorescence Spectra for QD in ODF

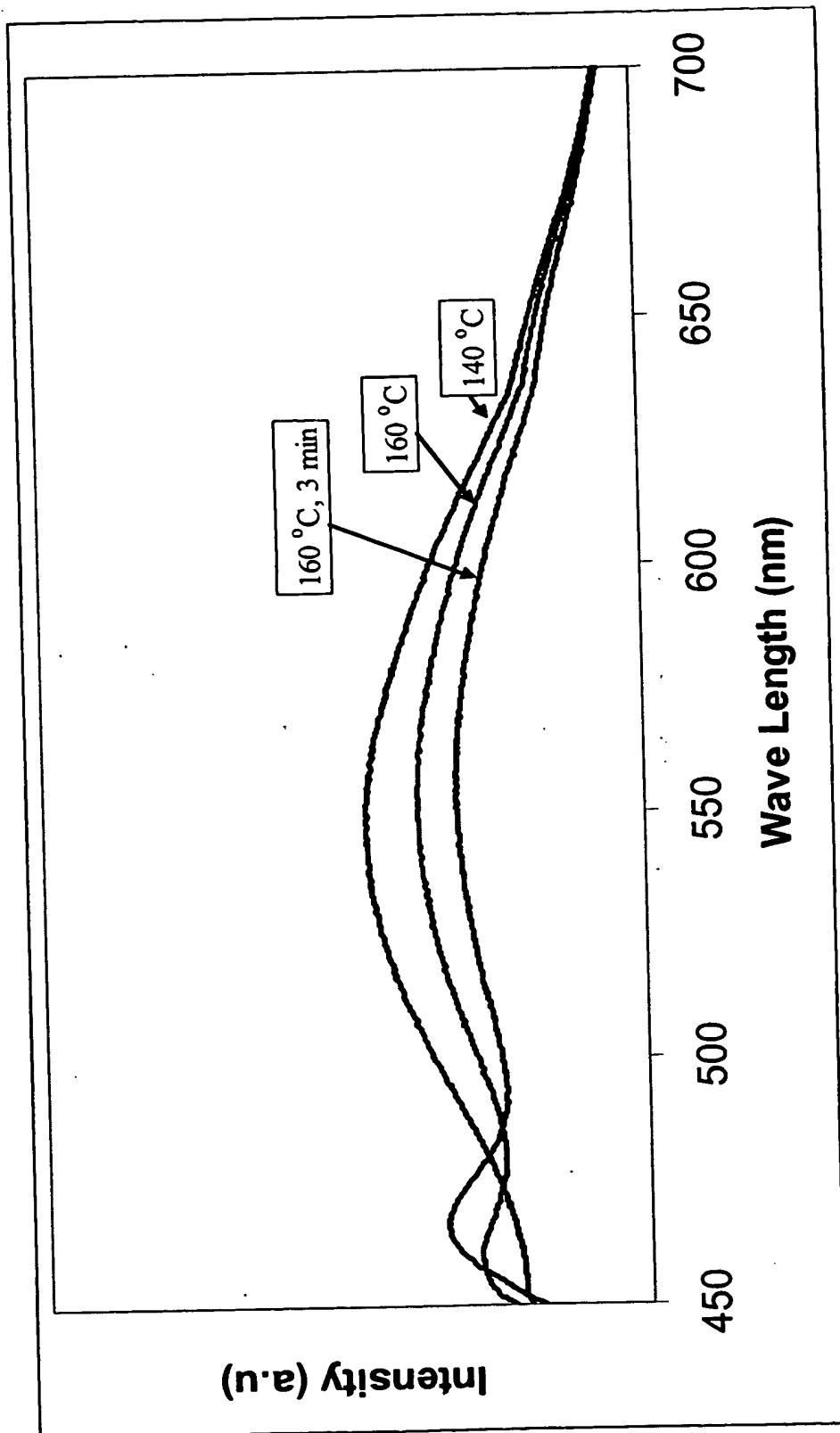


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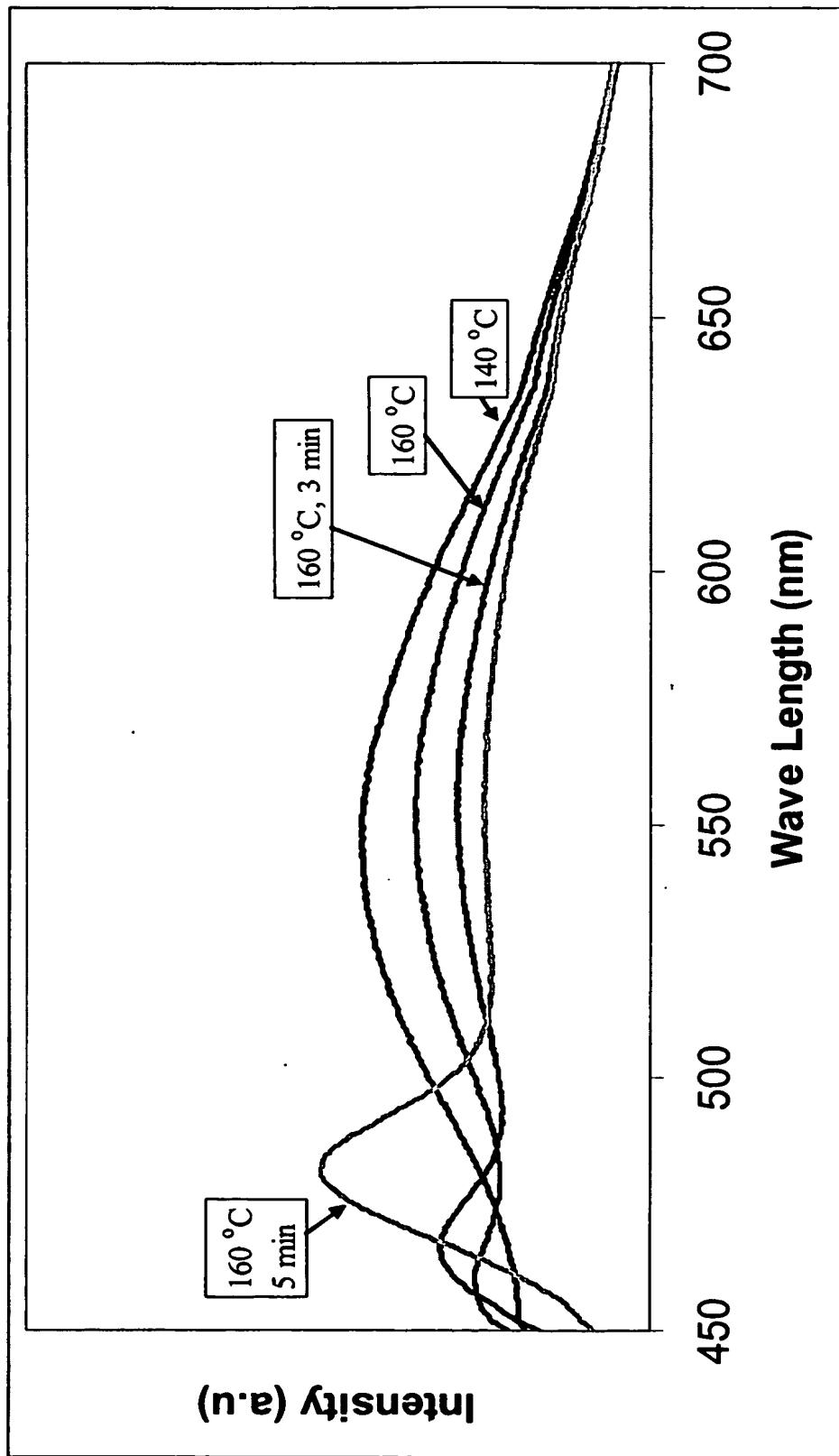
Fluorescence Spectra for QD in ODE



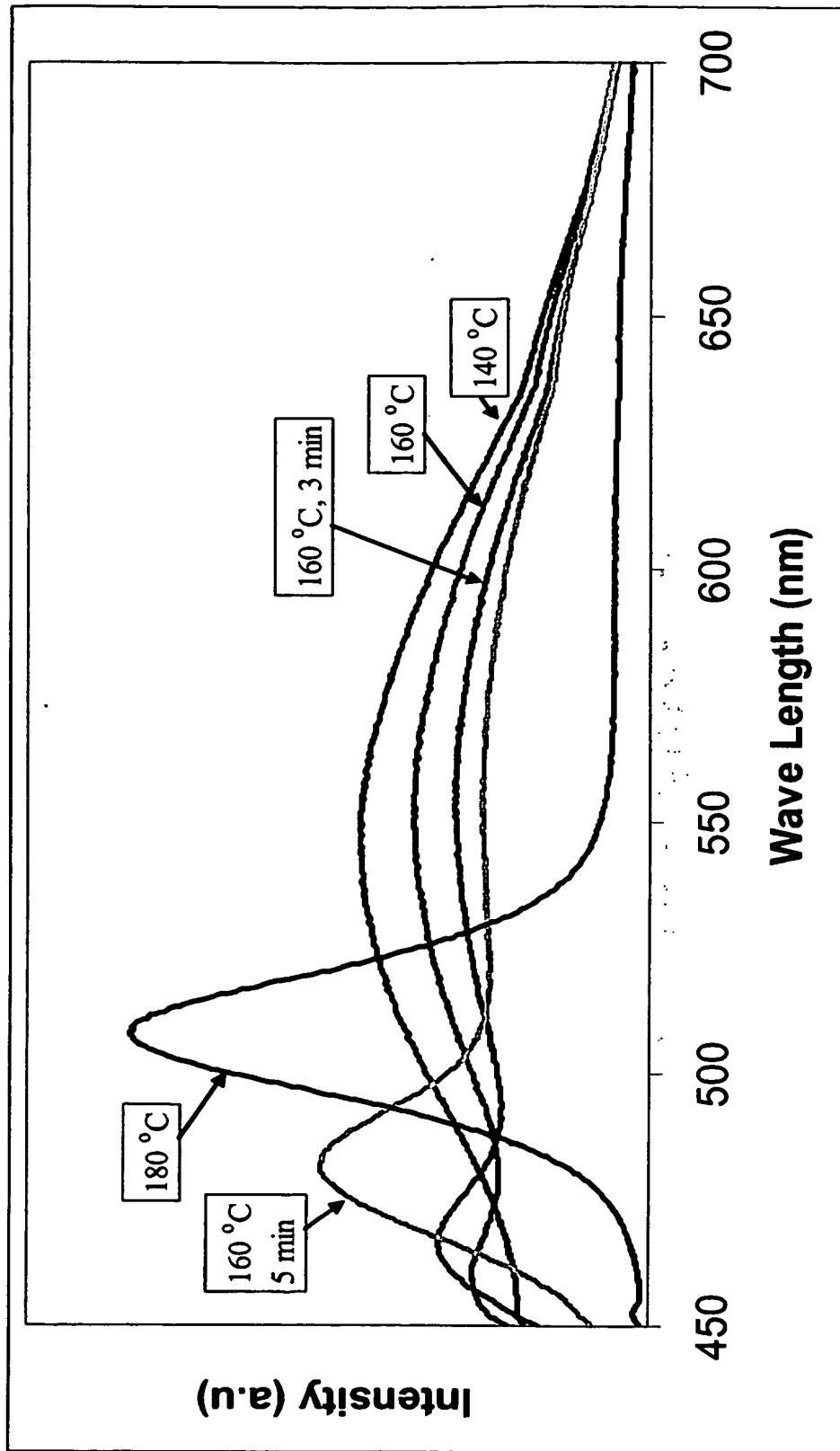
Fluorescence Spectra for QD in ODE



Fluorescence Spectra for QD in ODE

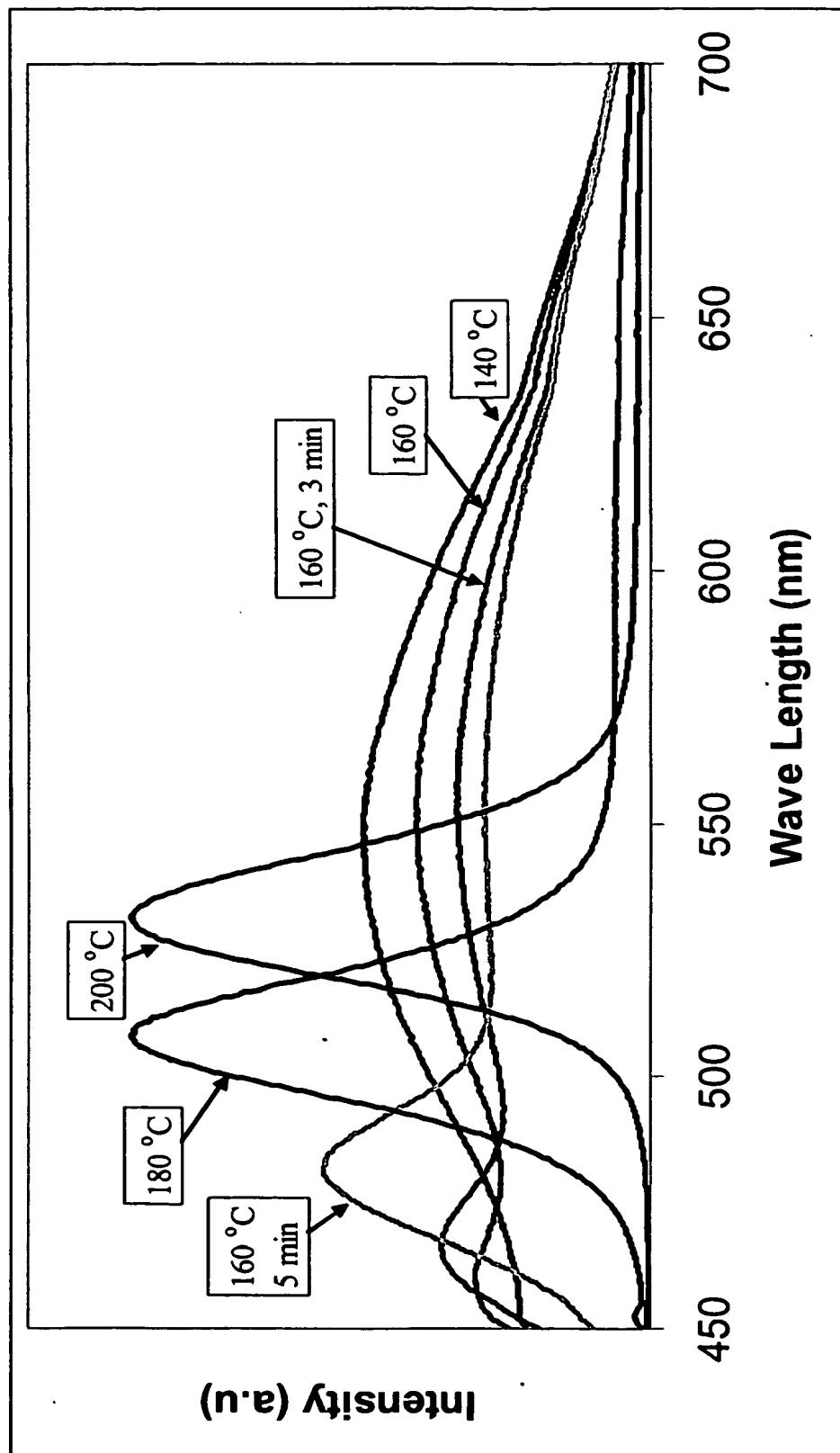


Fluorescence Spectra for QD in ODE

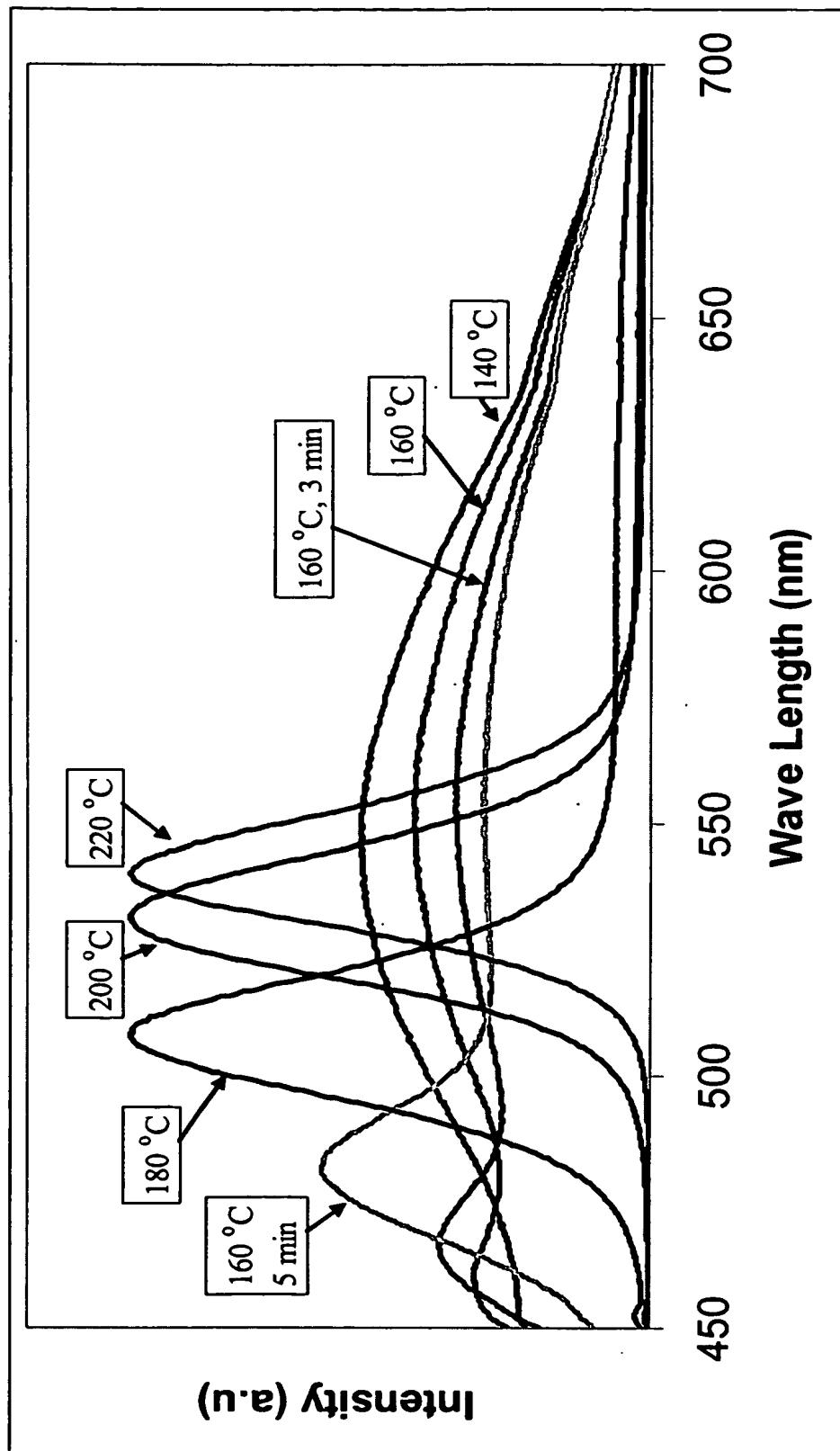


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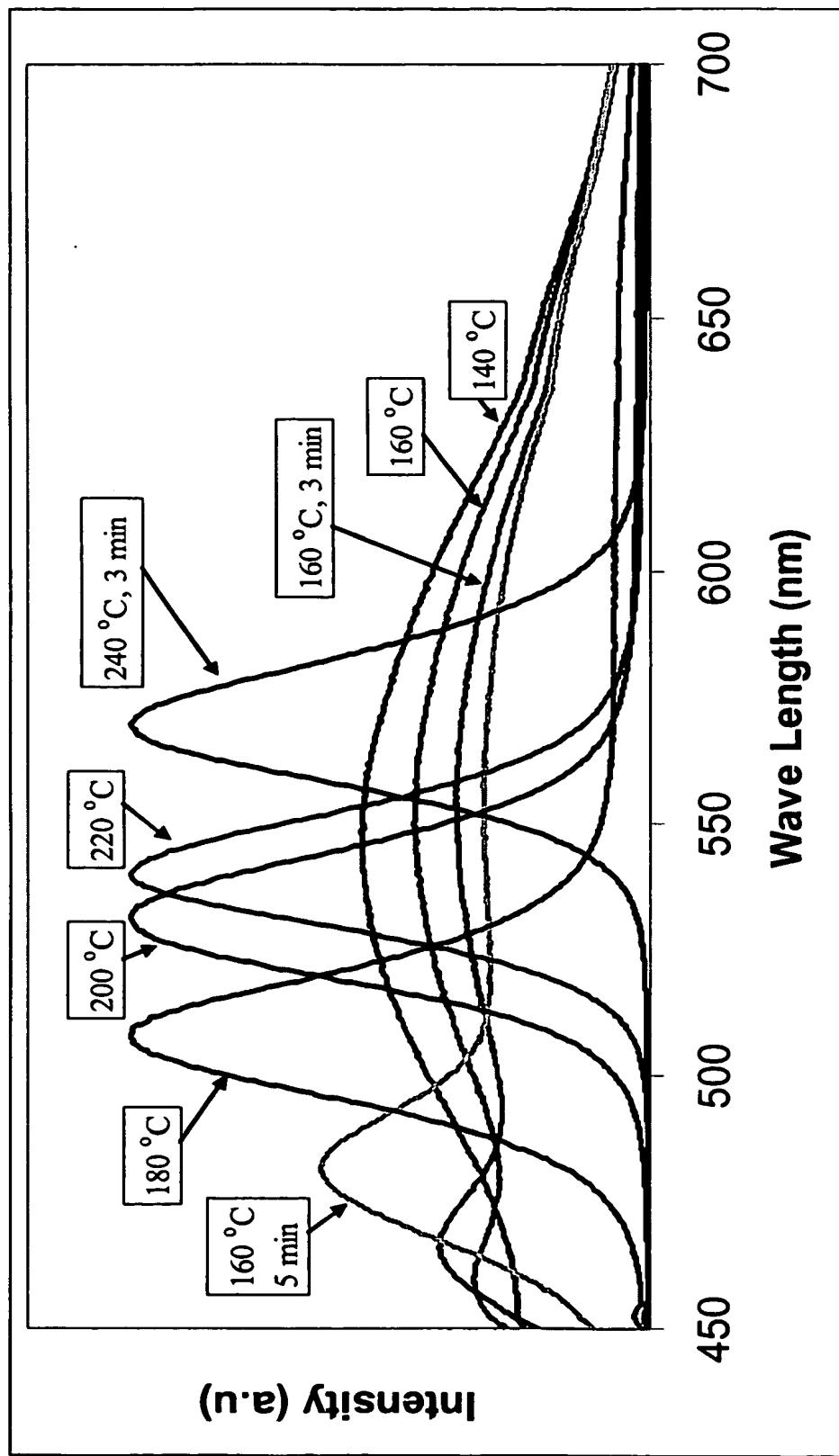
Fluorescence Spectra for QD in ODE



Fluorescence Spectra for QD in ODE



Fluorescence Spectra for QD in ODE

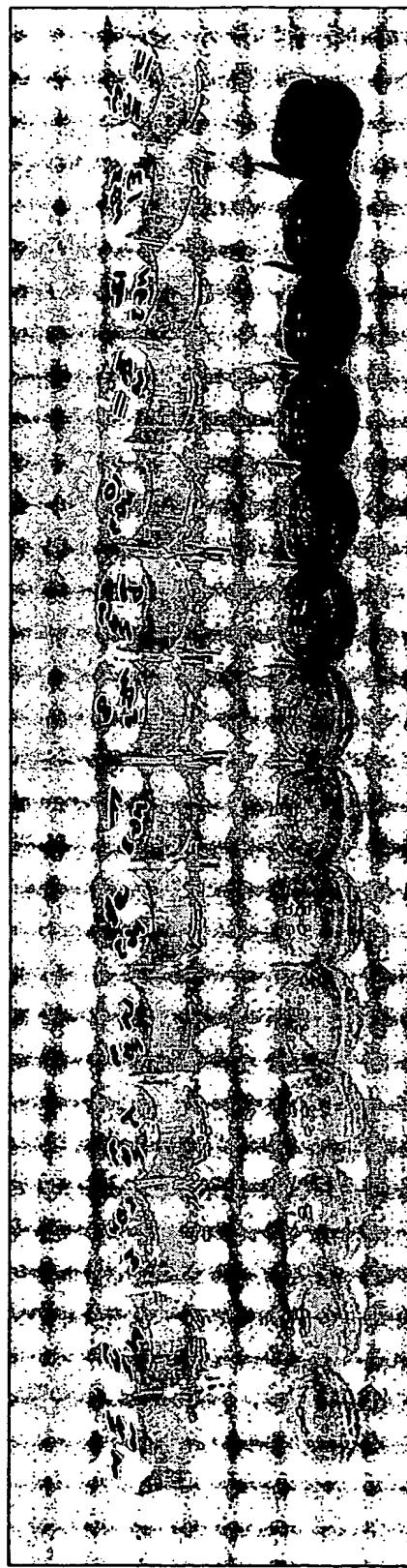


QD Synthesis in ODE

T (°C)	FWHM (nm)	Particle Size	Q.Y. (%)	[QD] mol/l	Product Yield (%)	Total Yield (mg/l)
180	30.4	2.2	22.5	0.00171	32.9	0.33
220	27.5	2.6	20.7	0.00308	59.2	0.59
230	26.8	2.8	20.9	0.00499	96.0	0.96
240	29.1	3.0	21.1	0.00507	97.6	0.97

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CdSe Quantum Dots in ODE



Increasing time and temperature ↑

Outline

- Introduction
- Large Batch Reactor
- Quenching Method
- New Solvents for Quantum Dot Synthesis
- Conclusions

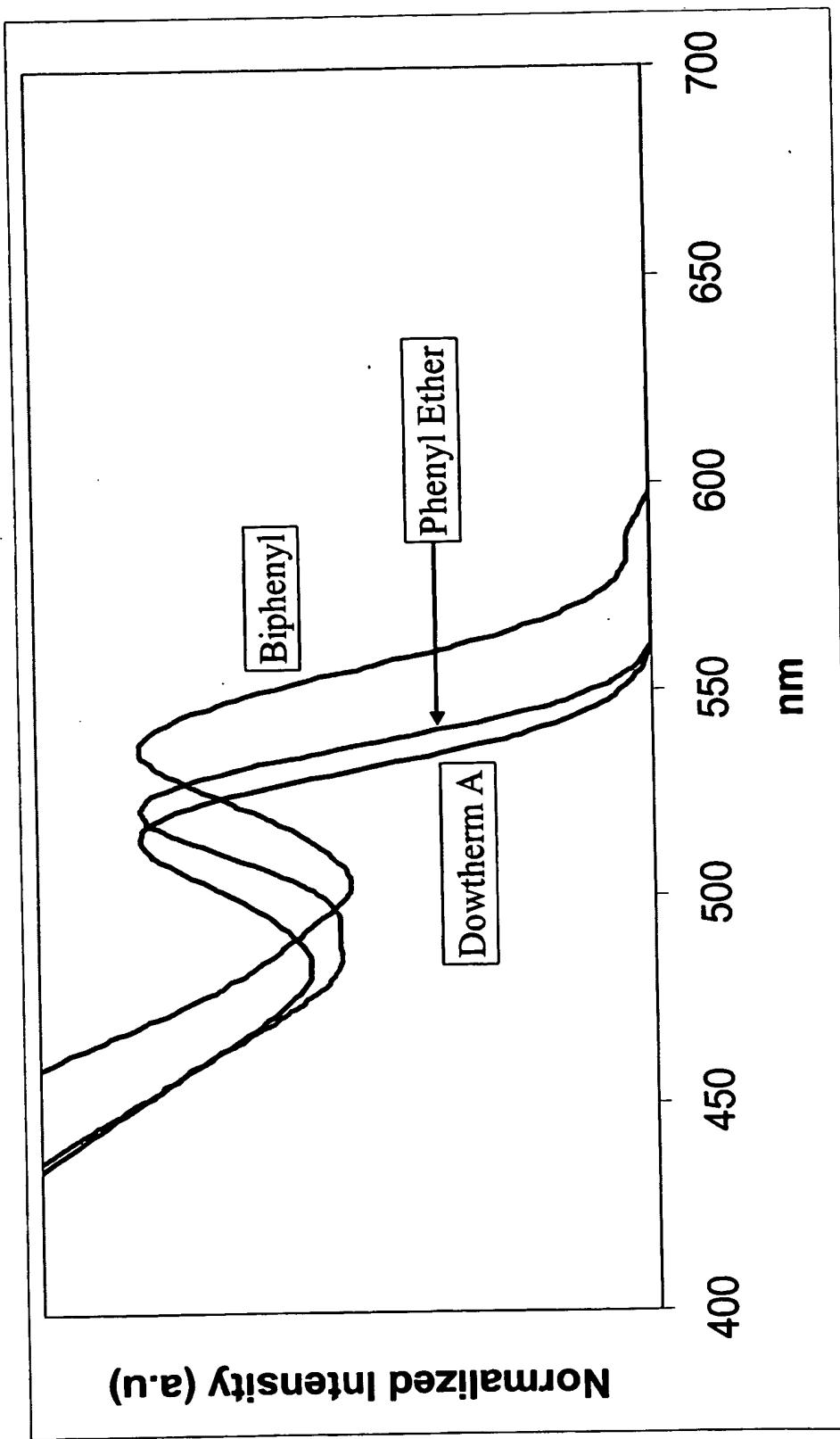
New Solvents for QD Synthesis

- Dowtherm A:
 - Phenyl ether/biphenyl blend used usually as a heating fluid
 - Supplied by Dow Chemicals
- Phenyl Ether: $(C_6H_5)_2O$
- Biphenyl: $C_6H_5C_6H_5$

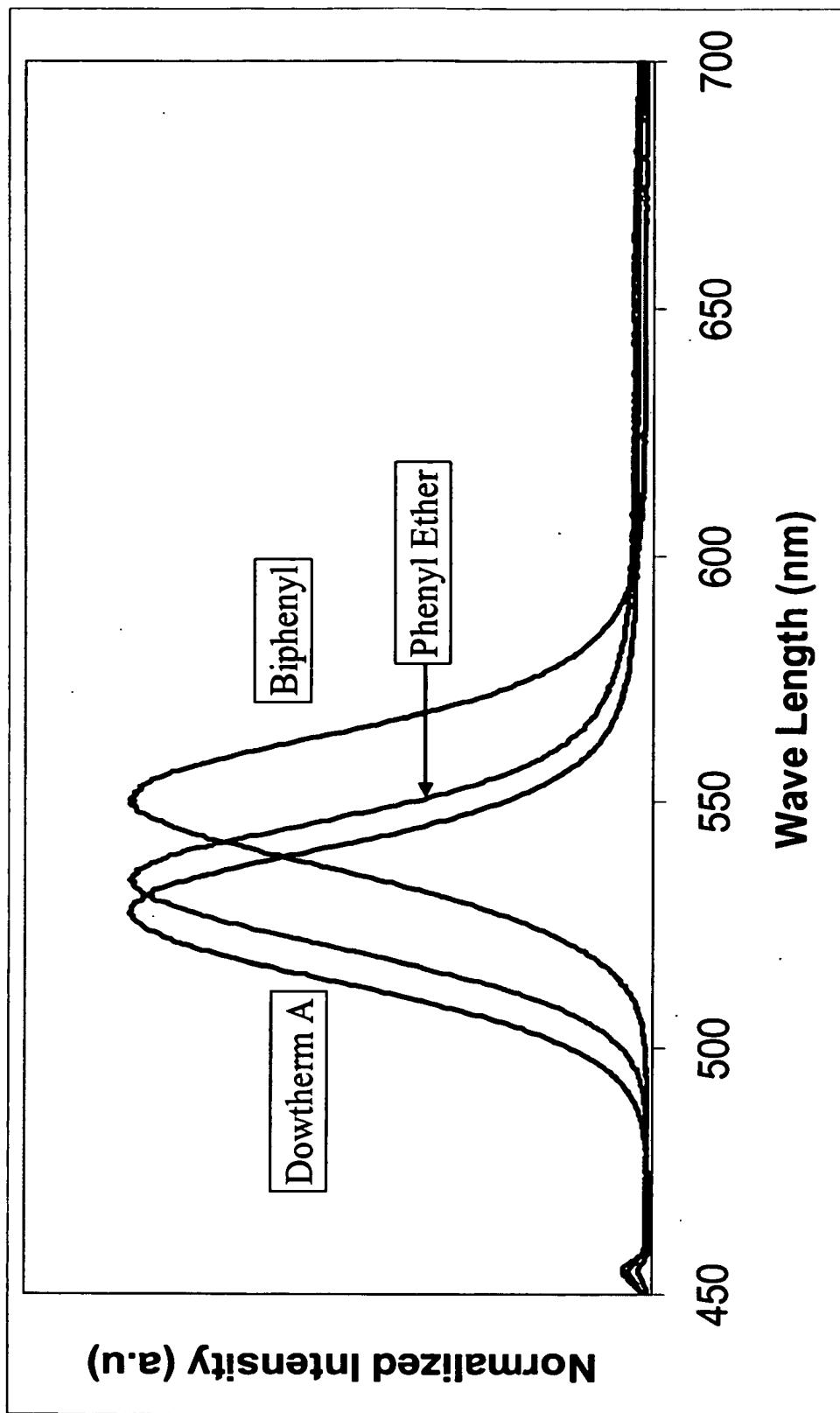
Solvents for QD Synthesis

Solvent	Price (\$/kg)	Melting Point (°C)	Boiling Point (°C)	Flash Point (°C)
TOPO	104	52		> 110
ODE	24	18	315	148
Dowtherm A	2	12	257	113

UV-VIS Spectra for QD in Different Solvents at 160 °C



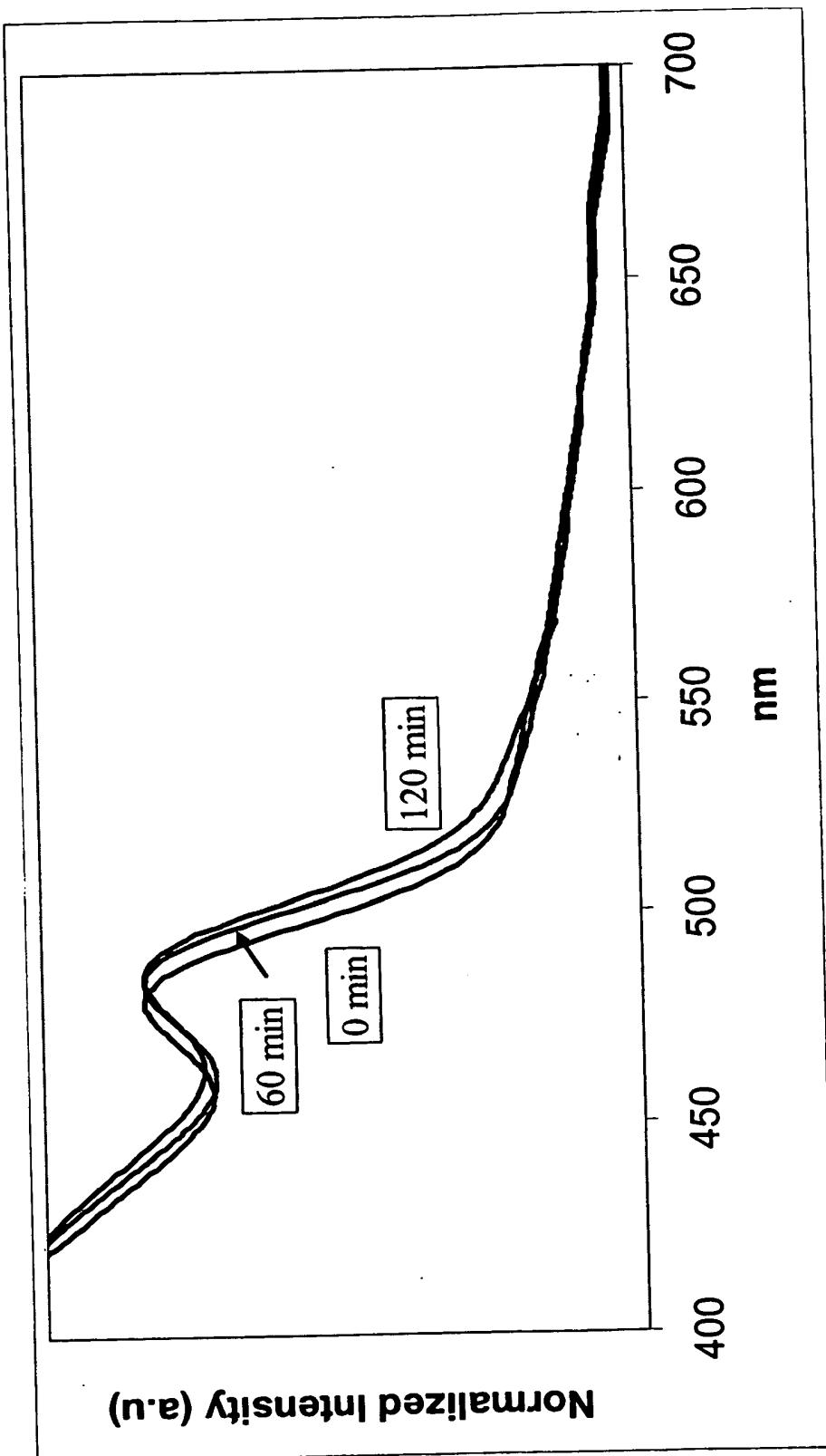
Fluorescence Spectra for QD in Different Solvents at 160 °C



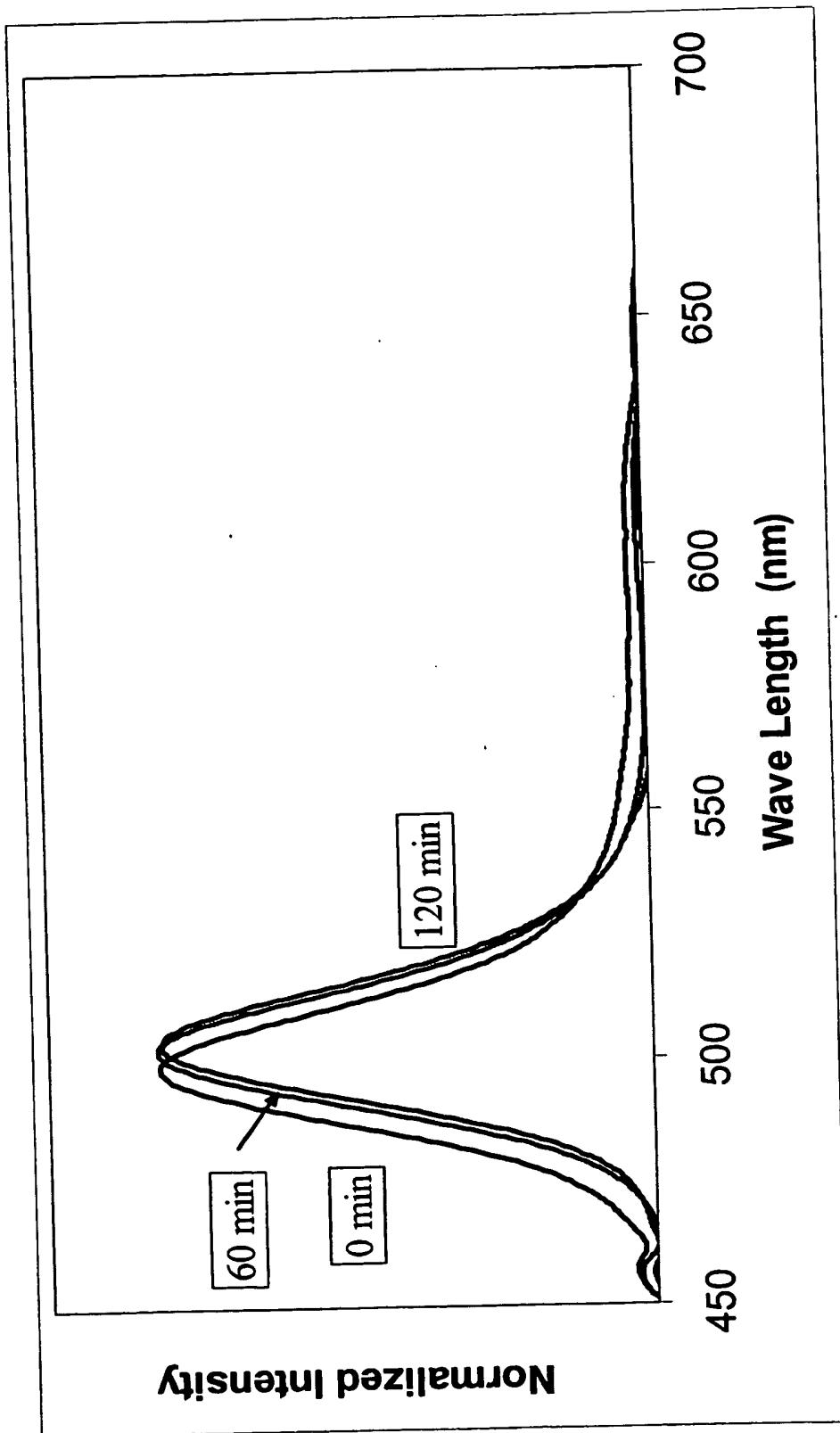
A Comparison of QD Synthesis in Different Solvents at 160 °C

Solvent	FWHM (nm)	Q. Y. (%)	Particle Size (nm)
Dowtherm A	32	8.8	2.4
Phenyl Ether	31	5.8	2.5
Biphenyl	33	6.6	2.8

UV-Vis Spectra of CdSe QD prepared in
Dowtherm A at 100 °C

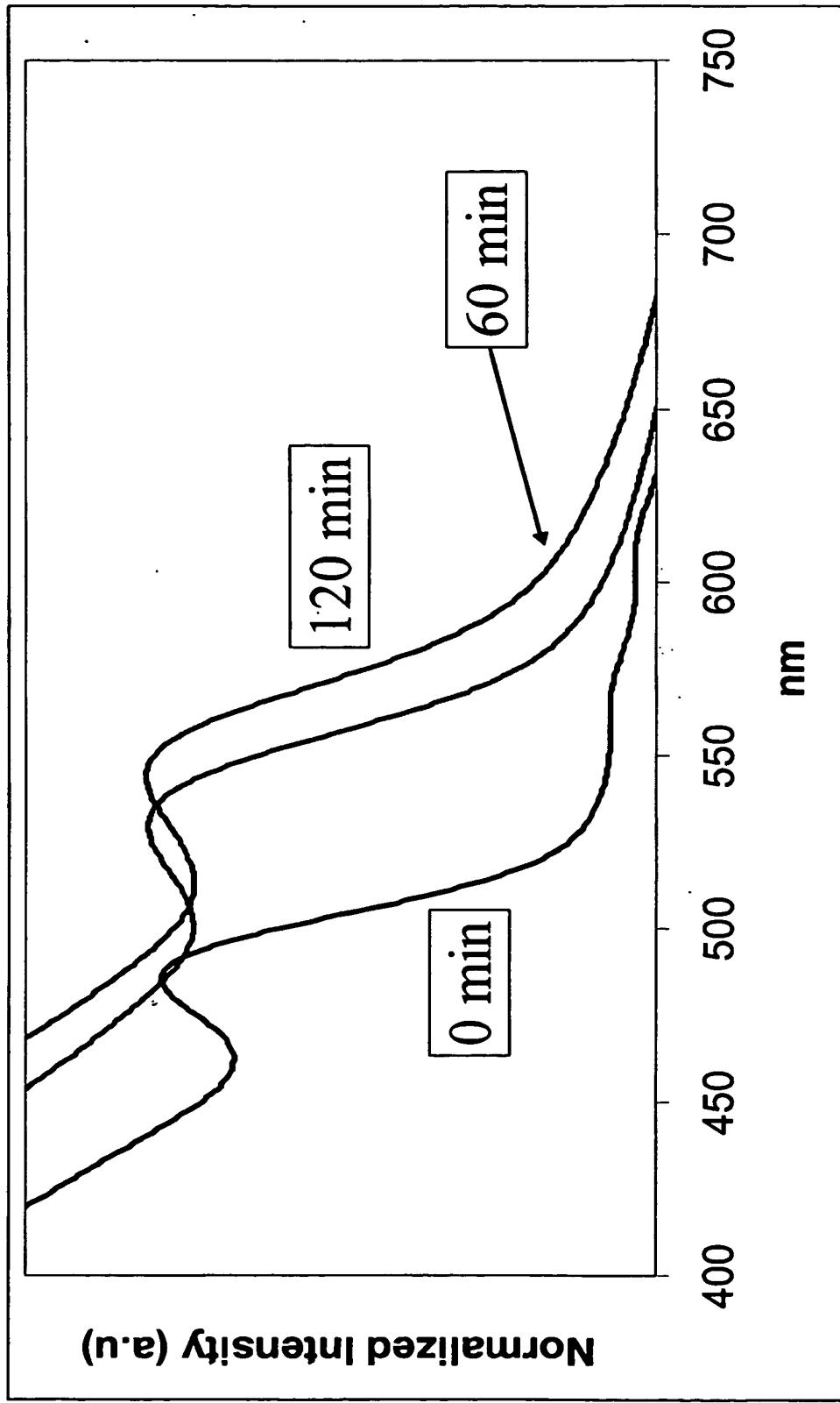


Fluorescence Spectra for QD in Dowtherm A at 100 °C

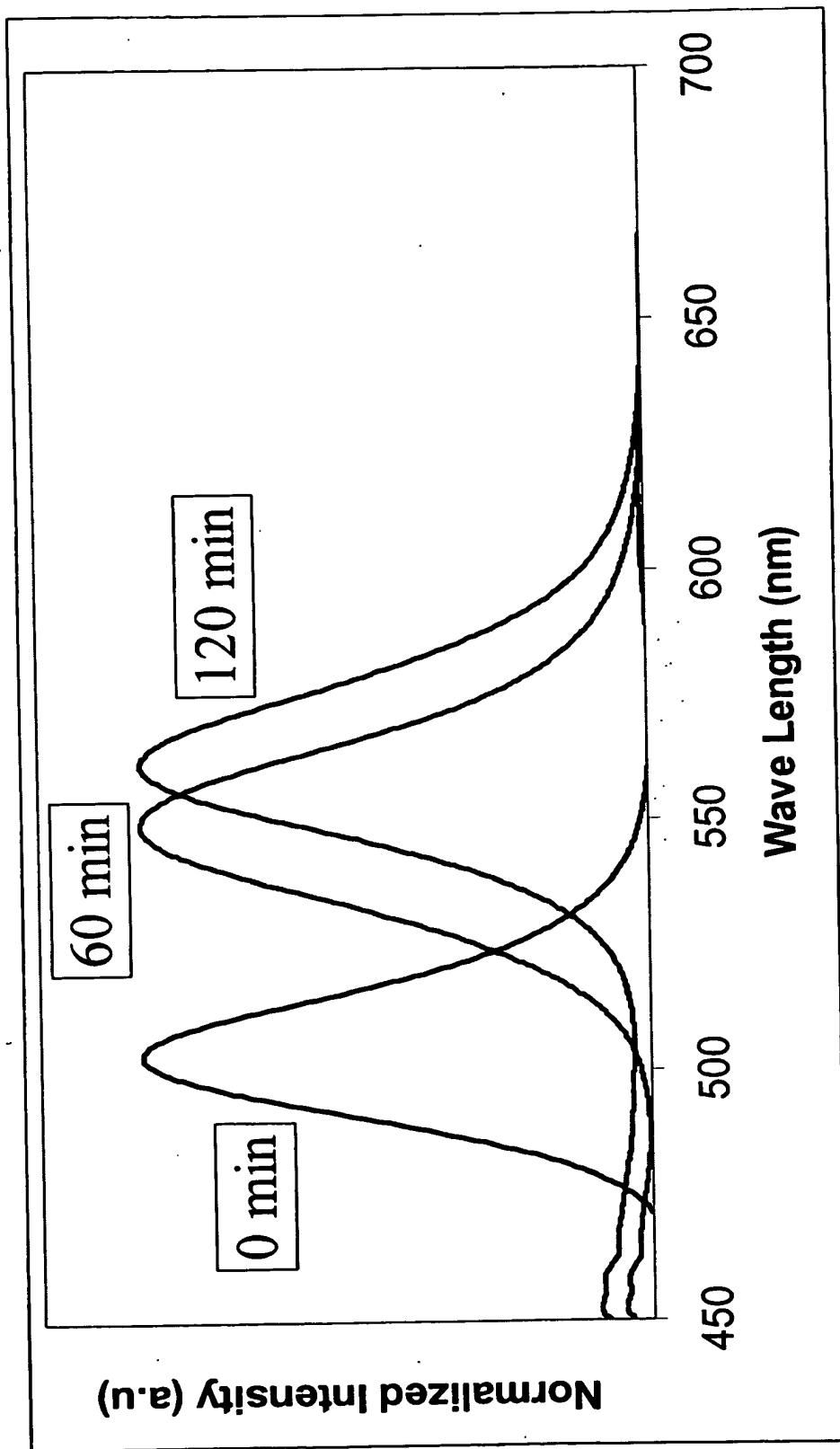


7

UV-Vis Spectra for QD in Dowtherm A at 160 °C



Fluorescence Spectra for QD in Dowtherm A at 160 °C



QD Growth in DT with Time at 160 °C

Time (min)	FWHM (nm)	Particle Size (nm)	[QD] mol/l	Product Yield (%)	Total Yield (mg/ml)
0	28.9	2.1	0.00207	30.7	0.40
10	38.5	2.4	0.002878	42.6	0.55
30	40.0	2.5	0.00382	56.6	0.73
60	36.7	2.7	0.005064	75.0	0.97
90	35.1	2.8	0.006214	92.0	1.19
120	34.2	3.0	0.006629	98.2	1.27

Summary and Conclusions

- Large reactor (1 L) to produce NPs
- Separation of nucleation and growth
(quenching with cold solvent)
- New low-price commercially-available
solvents for QDs synthesis

Acknowledgments

- Center for Biological and Environmental Nanotechnology (CBEN), [NSF EEC-0118047]
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 - Zuze Mu
 - Will Knowles
 - Vinit Murthy
 - Mike Nutt
- Catalysis and Nanomaterials Group

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